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# MECHANISM OF EPOXY MOISTURE EFFECTS

McDonnell Douglas Research Laboratories  
St. Louis, Missouri 63166

April 1977

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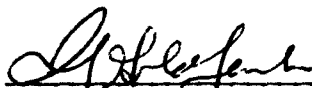
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This technical report has been reviewed and is approved for publication.



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FOR THE COMMANDER



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Based on mechanochemical considerations, the possibility for occurrence of irreversible stress-induced chemical changes in epoxy polymers exposed to humid environments cannot be excluded and is the main objective of this study. Internal reflectance Fourier transform infrared (FT-IR) spectra of tetraglycidyl diaminodiphenyl methane (TGDDM) cured with diaminodiphenyl sulfone (DDS) obtained before and after exposure to the combined effect of stress, elevated temperature, and moisture (STM), elevated temperature and moisture (TM) or stress and elevated temperature (ST) environments were used to obtain comparative evidence for irreversible chemical changes. These changes were compared with the infrared changes observed during the late stages of curing.

The results of eight different experiment series provide spectroscopic evidence indicating that exposure of epoxy specimens to STM and TM environments which greatly exceed anticipated service conditions leads to detectable rupture of chemical bonds in the polymer network. Internal swelling stresses are believed responsible for the observed bond cleavages. Spectral evidence indicates that, as expected, post-cure reactions are the most prominent chemical changes induced by exposure of epoxy specimens to the ST, SM, M and T environments. The infrared intensities of the bands attributed to the sulfone group are sensitive to chemical changes which suggests their potential use as molecular monitors within the epoxy network.

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## FOREWORD

This report is an account of the work performed by the McDonnell Douglas Research Laboratories, St. Louis, Missouri 63166, on the Mechanism of Epoxy Moisture Effects. The work was conducted under Contract No. F33615-76-C-5071, Project No. 2303, Task No. Q4, for the Air Force Materials Laboratory. The performance period was 01 January 1976-01 April 1977. This report was submitted in February 1977.

The work was performed in the Chemical Physics Laboratory, managed by Dr. C. J. Wolf. The principal investigator was Dr. R. L. Levy; co-investigators were Dr. C. J. Summers and Mr. D. L. Fanter; Dr. C. D. Craver, Chemir Co., assisted in infrared spectroscopy interpretation; and Dr. D. O. Helton, Midwest Research Institute, assisted in developing a process for resin purification. The project engineer was Dr. I. J. Goldfarb, AFML/MBP, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

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## SECTION I

### BACKGROUND

Structural nonmetallic (SNM) composites open a new dimension in aerospace materials technology. Their potential for improvements in system performance and dramatic weight/cost savings is recognized<sup>1-3</sup>, and extensive efforts for their incorporation in current aircraft designs are being extended jointly by DoD and the aerospace industry.<sup>2,3</sup> Resin matrix composites (RMC) based on epoxy resins and graphite fibers appear to offer the greatest promise in SNM technology. Such composites are of immediate interest as candidates for a number of components of present high-performance military aircraft (F-15, F-16, F-18) and are expected to assume a greater role in the future. However, demonstration of full life-cycle reliability is a prerequisite for their acceptance and rapid integration in load-bearing components of current aircraft.

It has been shown that the high-temperature properties of RMCs are adversely affected by absorbed atmospheric moisture.<sup>1-4</sup> The deleterious effect of atmospheric moisture on the properties of RMCs is attributed mainly to the so-called plasticization of the epoxy resin. This observation has prompted a number of studies devoted mainly to the physical aspects of epoxy moisture effects.<sup>2-4</sup> A comprehensive review of epoxy moisture effects was given by Browning.<sup>4</sup>

Two Air Force sponsored workshops<sup>2,3</sup>, encompassing a broad range of disciplines, were devoted to various aspects of RMC durability moisture/temperature problems. Distinct areas of study include the matrix-fiber interface, fiber-surface characteristics, resin matrix properties, rate of water diffusion, and dimensional stability. Specifically, the combined effects of stress, absorbed atmospheric moisture and thermal environments, which represent flight envelopes of advanced aircraft, were defined as areas of immediate interest.<sup>2,3</sup> Browning<sup>4</sup> stressed the need to study the neat resin matrix materials in order to differentiate between composite-structure problems and matrix-related problems. The plasticization mechanism<sup>2-5</sup> accounts well for the reversible and short-term aspects of the observed moisture effects. The possibility of other mechanisms being concurrently operative and possibly enhanced by the plasticization phenomena is of special interest. It has been postulated<sup>3</sup> that stress-induced,

irreversible chemical changes, the subject of this study, could cause a small but cumulative loss of properties. Mechanochemical considerations<sup>5,6</sup> suggest that two stages can be distinguished in considering the effect of stress at the molecular level:

- 1) stress applied to the polymer producing an increase in the inter-atomic distance and a change in the bond angles without causing bond rupture, and
- 2) stress-induced bond cleavage leading to formation of free radicals or other chemical species capable of further reaction.

The reasoning behind the bond-activation effect of stress is as follows. When a polymer chain is stretched, a number of deformation states are assumed to occur prior to bond cleavage. These deformation states are characterized by changes in interatomic distances and bond angles, which cause an increase in the potential energy of the molecule. The increased energy in the system reduces the energy required for chemical reactions, i.e., stress appears to decrease the activation energy required for a particular reaction.

At elevated temperatures, the probability for occurrence of stress-induced reactions is further enhanced. When the localized stress applied to a polymer chain exceeds a critical value, bond scission and the formation of free radicals occur. Under such conditions, a different mechanism is involved. The newly formed macroradicals can undergo a variety of reactions depending on the species present in their immediate environment.<sup>6</sup> Other processes which could lead to irreversible chemical changes in epoxy resins exposed to stress, elevated temperature, and moisture are:

- 1) Continued polymerization or cross-linking of the polymer network. Since cross-linking reactions that embrittle epoxies by inhibiting plastic flow during failure are diffusion controlled, the plasticizing effect of water enhances the molecular mobility at high temperature which facilitates further cross-linking reactions resulting in irreversible changes in mechanical properties.
- 2) The enhanced molecular mobility produced by water could increase high-temperature, oxidative, cross-linking reactions.
- 3) Internal stresses induced by swelling can cause bond rupture with the resulting network degradation effect.

The study described in this report is directed toward the possible irreversible chemical effects of stress, elevated temperatures, and moisture (STM) on the properties of epoxy resins. It is a continuation of the work performed under AFML Contract F33615-75-C-5144 and described in technical report AFML-TR-76-190.<sup>5</sup>

## SECTION II

### OBJECTIVES

The primary objective of this research program was to seek evidence for the occurrence of irreversible stress-induced chemical changes in moisture-containing epoxy resins at elevated temperatures. The possible effects of stress level, post-cure heating, acidic or basic environments, and concentration of curing agent on the observed chemical changes were considered of special interest for the elucidation of the mechanisms occurring during exposure of the epoxy resin to the combined effect of stress, elevated temperatures, and moisture (STM). The primary analytical technique used for detection of minor chemical changes in epoxy specimens was internal reflectance Fourier transform infrared (FT-IR) spectroscopy.

The epoxy resin system selected for these studies is based on tetraglycidyl diaminodiphenyl methane (TGDDM) cured with diaminodiphenyl sulfone.

The development of methods capable of detecting minor chemical changes in epoxy resins is a secondary objective of this program.

### SECTION III

### CONCLUSIONS

Difference FT-IR spectroscopy of epoxy specimens recorded before and after exposure to a given environment permits detection of the minor chemical changes induced in the polymer network by this environment. Qualitative spectroscopic evidence indicates that exposure of an epoxy resin to an autoclave STM and TM environments leads to detectable rupture of chemical bonds in the polymer network. The autoclave STM and TM environments, intended to provide accelerated aging, greatly exceed the anticipated service conditions. Spectral features indicative of such bond rupture were found to be independent of the applied tensile stress from 0-90 kg/cm<sup>2</sup>. Internal swelling stresses are therefore believed responsible for the observed bond cleavages. Spectral evidence suggests that post-cure reactions by residual epoxy groups with secondary amines and possibly by other reactive moieties are the most prominent chemical changes induced by exposure to the ST, SM, M, and T environments. Near-infrared difference spectra indicate that such reactions also occur in the STM environment. Following STM exposure, the spectral changes observed at 600-1800 cm<sup>-1</sup> that indicate bond rupture probably represent only the difference between bonds cleaved and bonds formed by post-cure reactions.

Immersion of epoxy specimens in acidic or basic aqueous solutions (pH 3-12) for 40 h does not induce significant spectral changes. Exposure of specimens, which had been immersed in acidic or basic solutions, to the STM environment shows no detectable increase in their susceptibility to the STM environment. Epoxy specimens exposed to stress and moisture (SM) at room temperature and a thermal spike did not exhibit significant spectral differences in comparison to specimens exposed to SM without thermal spiking.

Specimens containing different percentages of DDS show similar spectral patterns as a result of exposure to STM, indicating that DDS content does not alter the mechanism responsible for the observed changes.

Spectral evidence suggests that moisture absorbed by epoxy specimens at room temperature induces limited post-cure reactions possibly by relaxation of internal stresses. The intensities of the infrared bands attributed to the sulfone group, which is present in segments of the epoxy network originating in the DDS, exhibit sensitivity to changes in their immediate environment

suggesting their potential use as passive monitors or molecular probes within the epoxy network. The tentatively postulated rupture of the carbon-sulfur bond suggested in the first phase of this study<sup>5</sup> as one possible explanation for the observed changes in the sulfone bands appears incompatible with the experimental evidence obtained in this study phase.



## SECTION IV

### APPROACH

A detailed description of the approach taken in this research program is given in Technical Report AFML-TR-76-190<sup>5</sup> which describes the first phase of our work. A brief summary of the Approach Section from this report is included here along with descriptions of the items specifically pertinent to this report.

#### 1. RESIN SYSTEM SELECTION

The choice of a resin system for study in this program was based on the following criteria: the epoxy resin system must be chemically well-defined, and the system should be similar to those currently used in resin matrix composites.

Through consultation with Dr. I. J. Goldfarb, Project Engineer, and other AFML personnel, a two-component resin system consisting of MY-720 tetraglycidyl epoxy resin (Ciba Geigy) and diaminodiphenyl sulfone (DDS) as a curing agent was selected for the studies described in this report. This resin system represents the major ingredients of the neat resin of the well-known Narmco 5208 and Hercules 3501 graphite-epoxy laminates and therefore meets the requirement for similarity to the resins currently used for aircraft components.

#### 2. ANALYTICAL TECHNIQUES

The detection of minor chemical changes in cured epoxy resins is a difficult task because of their complex three-dimensional network and their insolubility in known solvents. This fact minimizes the number of useful chemical analysis methods and suggests that physical analytical methods applicable to solids are most suitable. Careful evaluation of the applicability of various physical analytical methods to the problems encountered in the detection of minor stress-induced chemical changes in cured epoxy resins led to the following conclusions:

- a) Infrared spectroscopy which is widely used in polymer analysis offers distinct advantages over other analytical methods for solid organic polymers.
- b) Fourier transform infrared spectroscopy aided by computer data analysis has the greatest potential for in situ detection of chemical changes and for providing clues on the mechanism of these changes.

- c) Internal reflection techniques must be used because the thin epoxy films required for infrared transmission over a broad spectral range are difficult to fabricate reproducibly and are too fragile for meaningful exposure to stress. Unfortunately, the internal reflection technique is restricted to observation of chemical changes occurring in the immediate vicinity of the surface.
- d) Special techniques for computer processing of the FT-IR spectra can enhance the potential of FT-IR for this application.

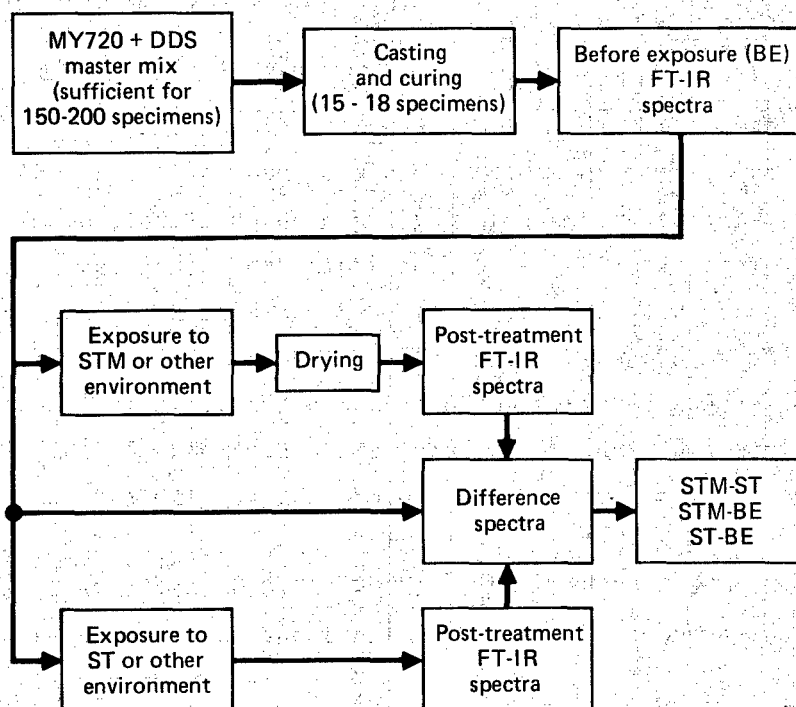
Discussions of the specific features of FT-IR, internal reflectance, and difference spectroscopy as they pertain to this work are given in the report describing the first phase of this study.<sup>5</sup>

The objective of the experimental approach was to expose the epoxy specimens to a variety of environments assuming that each series of experiments (environments) would provide complementary information on the operative mechanisms.

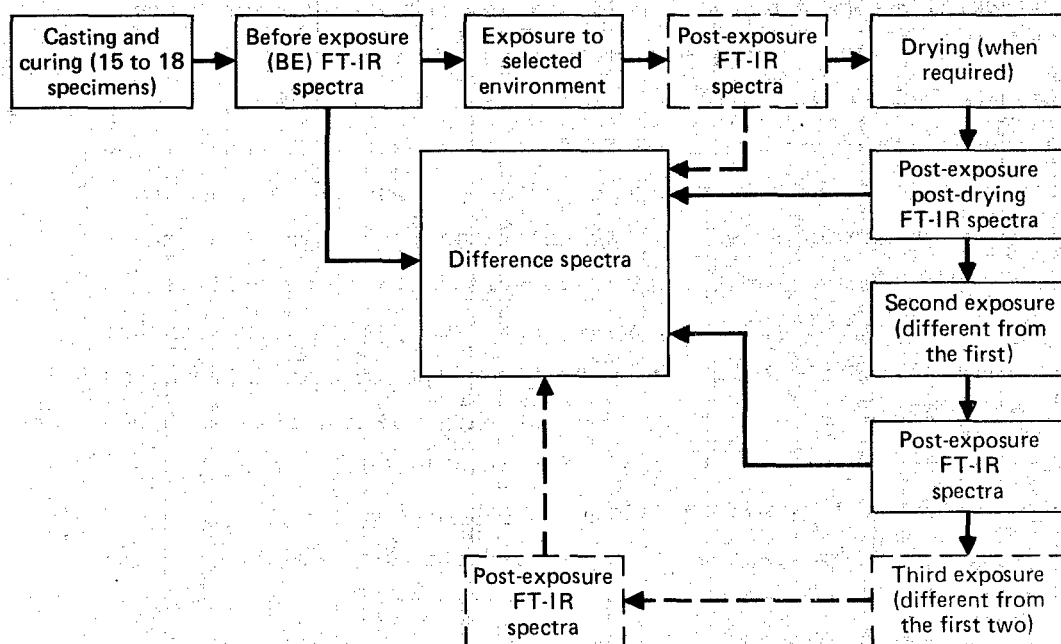
### 3. RESEARCH PLAN

The basic scheme of the research approach developed to obtain evidence for the combined effect of stress, elevated temperature, and moisture on epoxy specimens is illustrated in Figure 1.

Each set of experiments is designated by a series number or name (such as acid/base immersion or thermal spiking) consisted of a batch of 15-18 dogbone-shaped specimens cast and cured simultaneously. All specimens of a particular series were assigned individual numbers, and their internal reflectance FT-IR spectra were recorded before exposure and stored on magnetic tape. The specimens were then divided into groups, each group for exposure to a particular environment. The samples were dried following exposure to the STM environment as indicated in Table 1. Following exposure, the internal reflectance FT-IR spectra were again recorded and stored on magnetic tape. Difference spectra were obtained by processing on a Xerox Sigma-9 time-share computer. The various exposure variables of the more important series of experiments are summarized in Table 1. The stress levels applied in the exposure of the specimens to the various environments were selected to cover a range of stress values from  $< 30$  to  $90 \text{ kg/cm}^2$  (the estimated elastic limit  $\approx 30 \text{ kg/cm}^2$ ) by placing them in a stress rig.<sup>5</sup>



**Figure 1** Overall experimental sequence for the detection of moisture- and stress-induced chemical changes in epoxy resins



**Figure 2** Illustration of modified sequence for the experimental approach

**TABLE 1 RECORD OF ENVIRONMENTAL EXPOSURES FOR THE MAIN SERIES OF EXPERIMENTS**

Series	Pre-exposure spectra	Exposure	Post-exposure spectra	Exposure	Spectra
Acid/base immersion and STM	A	pH 3, 40 h, D <sub>1</sub>	A	STM	A
	A	pH 5, 40 h, D <sub>1</sub>	A	STM	A
	A	pH 7, 40 h, D <sub>1</sub>	A	STM	A
	A	pH 9, 40 h, D <sub>1</sub>	A	STM	A
	A	pH 12, 40 h, D <sub>1</sub>	A	STM	A
	A	Control, not immersed		STM	A
	A	Control, not immersed		ST	A
	A	Control, not immersed		TM	A
Thermal spiking and SM	A	SM, 100°C spikes	A	D <sub>2</sub>	A
	A	SM, 135°C spikes	A	D <sub>2</sub>	A
	A	SM, Control	A	D <sub>2</sub>	A
	A	M, 135°C spikes	A	D <sub>2</sub>	A
	A	M, Control	A	D <sub>2</sub>	A
	A	M, Control	A	D <sub>2</sub>	A
	A	M, Control	A	D <sub>2</sub>	A
Post-cure heating and STM	A	185°C, 2 h	A	STM, D <sub>3</sub>	A Tr
	A	200°C, 2 h	A	STM, D <sub>3</sub>	A Tr
	A	Control	A		Tr
	A	S (90 kg/cm <sup>2</sup> )	A		Tr
	A	177°C, 10 h	A	STM, D <sub>3</sub>	A Tr
	A	177°C, 10 h	A	STM, D <sub>3</sub>	A Tr
	A	177°C, 10 h	A	STM, D <sub>3</sub>	A Tr
	A	177°C, 10 h	A	ST, D <sub>3</sub>	A Tr
Stress effects in STM	A	STM, 16 kg/cm <sup>2</sup>	A Tr		
	A	STM, 30 kg/cm <sup>2</sup>	A Tr		
	A	STM, 60 kg/cm <sup>2</sup>	A Tr		
	A	STM, 90 kg/cm <sup>2</sup>	A Tr		
	A	Control	A Tr		
Effects of curing agent ratio	A	17 phr DDS, STM	A		
	A	17 phr DDS, ST	A		
	A	23 phr DDS, STM	A		
	A	23 phr DDS, ST	A		
	A	27 phr DDS, STM	A		
	A	27 phr DDS, ST	A		
	A	35 phr DDS, STM	A		
Transmission spectra of STM and ST exposed coupons	Tr	17 phr DDS, STM	Tr		
	Tr	17 phr DDS, ST	Tr		
	Tr	23 phr DDS, STM	Tr		
	Tr	23 phr DDS, ST	Tr		
	Tr	27 phr DDS, STM	Tr		
	Tr	27 phr DDS, ST	Tr		
	Tr	35 phr DDS, STM	Tr		
	Tr	35 phr DDS, ST	Tr		

Notes: unless noted otherwise:

Coupons were produced from one mix of M4720 + 23 phr DDS

S = stress, 30 kg/cm<sup>2</sup>, 10 h

T = temperature, 135°C, 10 h

M = moisture, 100% RH

A = atr spectrum recorded

Tr = transmission spectrum recorded

D = dried, D<sub>1</sub>: 110°C, nitrogen atmosphere for 10 h

D<sub>2</sub>: 90°C, nitrogen atmosphere for 3 h

D<sub>3</sub>: stored in vacuum dessicator for 96 h

A somewhat different scheme which was used in many of the experimental series is shown in Figure 2. It consists of consecutive exposure of a given specimen to different environments. Examples of such consecutive exposures are exposure of the acid- or base-immersed specimen to the STM environment and exposure of the post-cure specimens to the STM environment.

## SECTION V

### EXPERIMENTAL

#### 1. SAMPLE FABRICATION

The epoxy samples used to perform the experiments for this study were produced by a casting procedure developed at MDRL.<sup>5</sup> Silicone rubber molds (General Electric RTV-664) were made from stainless steel patterns which had been machined and polished to the dimensions and surface finish required to meet the need for environmental exposure and internal reflectance infrared analysis. The epoxy resin used for casting was prepared by mixing the Ciba Geigy MY-720 resin and the DDS (Eporal, Ciba-Geigy) at 150°C to dissolve the DDS; the hot solution was then degased in vacuum and poured into the preheated RTV molds. The resin was cured within the molds and removed after the curing cycle. After curing, the samples were stored in a dessicator and were not subjected to polishing or machining; special care was taken to avoid any organic contamination.

#### 2. STM, ST, TM, SM AND M ENVIRONMENTAL EXPOSURE

Exposure of samples to combined stress, temperature, and moisture (STM) was conducted by clamping the sample in a spring-loaded stress rig, setting it to the desired stress level and placing it in an autoclave at 135°C. Stress and temperature (ST) exposure was conducted by stress-loading the samples within a nitrogen-purged oven at 135°C. Samples exposed to temperature and moisture (TM) were placed, unstressed, in the autoclave. Exposure to stress and moisture (SM) and moisture (M) environments at room temperature was conducted by placing stressed specimens in a 100% relative humidity atmosphere. During exposure to stress sufficiently high to cause sample creep, the relaxation of the spring in the stress rig resulted in a slight reduction of the stress level. Therefore, samples exposed to STM at higher stress levels (60-90 kg/cm<sup>2</sup>) were periodically removed from the autoclave, and the stress was readjusted to the desired level. To minimize the effects of rapid cooling of moisture-saturated samples and prevent the formation of water inclusions, samples removed from the autoclave were placed immediately in the nitrogen-filled oven, maintained at 135°C for 5 min, and then cooled slowly.

### 3. DDS RATIOS

Samples used during the experimental work of the first phase of this study<sup>5</sup> were prepared primarily from a resin containing MY720 plus 27 parts per hundred (phr) DDS. During the present contract period, samples were prepared primarily from a resin containing MY720 plus 23 phr DDS which is closer to the DDS concentration of a commercial graphite-epoxy prepreg formulation (Narmco 5208). A set of specimens containing 17, 23, 27 and 35 phr DDS were cast for the experiments designed to determine the effects of DDS concentration on the susceptibility of the epoxy resin to the STM environment.

### 4. ANGLE OF INCIDENCE OF THE INTERNAL REFLECTION PLATE

The angle of incidence of the infrared beam with respect to the internal reflection plate was changed from 70° to 80°. This change was made to obtain a shift of the background absorption envelope so that lower background absorbance in the 600-800  $\text{cm}^{-1}$  range is observed permitting slightly improved reliability of the data in this spectral range. However, an 80° angle of incidence results in a lower depth of penetration of the beam into the sample<sup>7</sup> and hence a somewhat lower intensity of the spectra. The difference spectra obtained by subtraction of lower intensity internal reflection spectra show the same features but with smaller values for the absorption gradient  $\Delta A$ .

### 5. DIFFERENCE FT-IR SPECTROSCOPY OF VARIOUS CURING STAGES

A small quantity of uncured resin mix containing 27 phr DDS was placed on an internal reflection KRS-5 plate. The FT-IR internal reflection spectrum was then recorded at zero curing time. The plate and the plate holder were then placed in an oven which was preheated to the desired temperature; the specimens were kept at this temperature for a predetermined period of time, i.e., 15 or 45 min, and removed from the oven; and the spectrum was recorded again. This procedure was repeated 12 times during the total curing time of 315 min. The chemical changes occurring either during consecutive stages of curing or between any two stages were observed by difference spectroscopy of spectra representing stage-n minus stage n-x, where x is the difference in the stage numbers.

### 6. CONDITIONS OF THE THERMAL SPIKING EXPERIMENT

The thermal spiking case refers to rapid heating for a short duration of a specimen exposed to ambient temperature environments such as stress and

moisture (SM) or moisture only (M). Figure 3 summarizes results of exposure of two specimens to SM combined with three thermal spikes up to 135° and 100°C respectively and exposure of two control specimens to SM and M without thermal spikes.

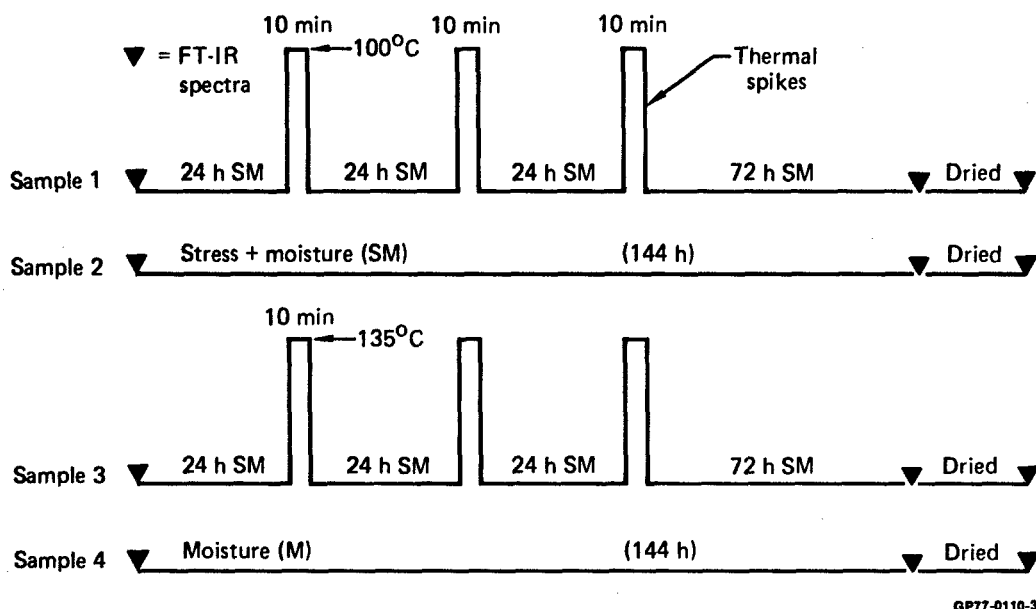


Figure 3 Schematic record of sample exposure to SM, M, and thermal spiking environments

## 7. ACID/BASE IMMERSION

Five solutions, pH 3, 5, 7, 9 and 12, were prepared from hydrochloric acid, distilled water, and potassium hydroxide. Spectra of five epoxy specimens were recorded before any exposure, and then one sample was immersed in each solution for 40 h. The samples were dried 3 h at 110°C in nitrogen and their FT-IR spectra were recorded. The five samples plus one control were then exposed to STM. Other control specimens were exposed to ST, TM and T.

## 8. SPECTROMETRIC CONDITIONS

Infrared spectra were recorded on a Fourier transform infrared spectrometer (Digilab model FTS-20). Interferometric data from 200 repetitive scans was recorded, transformed, and recorded on digital magnetic tape. Internal reflectance data were obtained with a internal reflectance attachment (Harrick model 4XTBCVA) with a sample holder containing a KRS-5 plate. Epoxy specimens



were clamped against the plate using a torque wrench set at 0.45 N·m (0.33 ft lb) to ensure repeatable pressure. Backgrounds of the KRS-5 plate were recorded immediately prior to obtaining spectra of each specimen.

Infrared spectra are recorded on a digital tape recorder (Kennedy model 9700) at 315 bits per cm. The data were then transferred to 630 bits/cm tapes and processed by a time-shared computer (Sigma-9) via an interactive CRT computer terminal (Tektronix).

## SECTION VI

### RESULTS AND DISCUSSION

In this study, evidence for occurrence of mechanochemical changes in epoxy resins was sought by the difference between FT-IR spectra obtained before and after exposure of epoxy specimens to a particular environment. It is assumed that even minor mechanochemical changes might have a cumulative deleterious effect on the long-term properties of epoxy resins. Therefore, the ability to detect minor chemical changes in a complex three-dimensional epoxy network is of special concern. In principle, any mechanochemical change which occurs to an extent exceeding the limits of detectability of the FT-IR spectrometer should be manifest in the difference spectrum. However, the limits of detectability in this case cannot be expressed simply in terms of instrument sensitivity and intensity of the infrared band representing the moiety undergoing change because the infrared spectrum of a complex polymer network usually consists of broadened and extensively overlapped bands.

Changes of intensity observed in the difference spectrum at a particular frequency could represent the sum of the individual changes occurring in the different bands absorbing at that frequency. The limits of detectability are, therefore, dependent on the detailed knowledge of spectral contributions of each chemical group and the intermolecular interactions in the network. Obtaining such detailed knowledge for a cured tetraglycidyl epoxy is obviously beyond the scope of this work.

To obtain information on the minor mechanochemical changes taking place in the epoxy network despite the above mentioned limitations, we developed an experimental approach which relies on three ingredients:

- 1) Reliance on changes in the stronger bands of the infrared spectrum;
- 2) Establishing an overall direction for the infrared changes induced by the curing process in the late stages of curing; and
- 3) Correlation of changes induced by different environments.

The reliance on the stronger bands of the spectrum was chosen because of their negligible dependence on contributions from overlapping bands and their greater detectability. The establishment of an overall direction for the infrared changes occurring during the late stages of curing was developed as an interpretative device from which conclusions can be derived for the general character

of the changes induced by a particular environment without knowledge of the exact reasons for the observed change. In this approach, all the changes that accompany the late stages of curing establish a direction for the infrared changes which reflect the progress of the curing process, i.e., the incorporation of new molecules into the network or further reactions of molecules already partly reacted. More important, by establishing this positive direction, we can detect changes which point to the opposite direction, i.e., changes which reflect degradation of the network caused by mechanochemical bond cleavages. Finally, the correlation of infrared changes observed in different series of experiments provides the broader information base required for better understanding of the processes involved.

#### 1. RELEVANT GENERALIZATIONS FOR INFRARED CHANGES OBSERVED DURING POLYMER CURING

The expected infrared spectral changes which accompany polymerization of polyfunctional monomers are:

- 1) The infrared bands which decrease at the fastest rate are usually attributable to the reactive groups consumed during polymerization. In cross-linked networks derived from polyfunctional monomers, these bands will not go to zero absorbance even in stoichiometrically balanced systems because of incorporation of monomer units in positions which inhibit further reaction. Absorption of low-molecular-weight solvents or atmospheric moisture plasticize or swell the rigid network permitting further reactions. These reactions embrittle the polymer and can cause internal stresses accompanied by bond rupture when the plasticizing agent is removed by drying. Thus a spectrum of a sample obtained after elimination of the plasticizing conditions may still show that reactive functional groups were reduced while indicating other spectral changes which point to bond rupture.
- 2) Bands which are highly sensitive to the mass of the substituents would be expected to decrease at a faster rate than bands which are reduced by the general broadening that accompanies polymerization.
- 3) Most bands which represent unreactive portions of the molecule not participating in the reaction show broadening and decrease in intensity.

- 4) Bands representing functional groups which enter into intermolecular interactions restricting their normal vibrations change at a rate faster than the bands considered in 3).
- 5) Infrared bands representing the newly formed bonds in the network should in principle show an increase at a rate similar to the rate of decrease of the bands representing the reactive groups. However, because monomer units are incorporated in different network positions, certain new bonds give rise only to a broad absorption which cannot be defined as a band.

## 2. ABSORPTION BANDS IN INTERNAL REFLECTANCE INFRARED SPECTRA

In comparison to spectra obtained by infrared transmission, the internal reflection spectra exhibit certain differences in the relative intensities of the bands. These differences in relative intensities arise mainly because of the change in the depth of penetration of the beam into the sample as function of the frequency.<sup>7</sup> The internal reflectance spectra of the individual components of the epoxy resin used in this study are shown in Figure 4 together with spectrum of their uncured mixture and a spectrum of the cured specimen. The relative contributions of the DDS and the MY-720 sections of the polymer network to the infrared spectrum of uncured and cured resin can be easily observed. The assignments of the molecular origins for the major bands appearing in the infrared spectra of the MY-720, DDS and the cured resin<sup>8-11</sup> are summarized in Table 2 including remarks on the diagnostic value of the individual bands and the direction of changes observed in the curing sequence or the exposure to STM. The two bands that exhibit the greatest sensitivity to changes in the network environment are the sulfone bands at 1102 and 1140  $\text{cm}^{-1}$ . As such they require special consideration. As an aid to understanding the behavior of these bands in different environments, a collection of infrared spectra of organic compounds containing the sulfone group was compiled.<sup>9-11</sup> The positions of the band maxima for a selected group of bands were measured for each spectrum and are summarized in Figure 5.

## 3. SPECIFIC OBJECTIVES AND RESULTS OF THE INDIVIDUAL SERIES OF EXPERIMENTS

The experimental work described in this report was performed in eight series of experiments, each designed and performed with a specific objective.

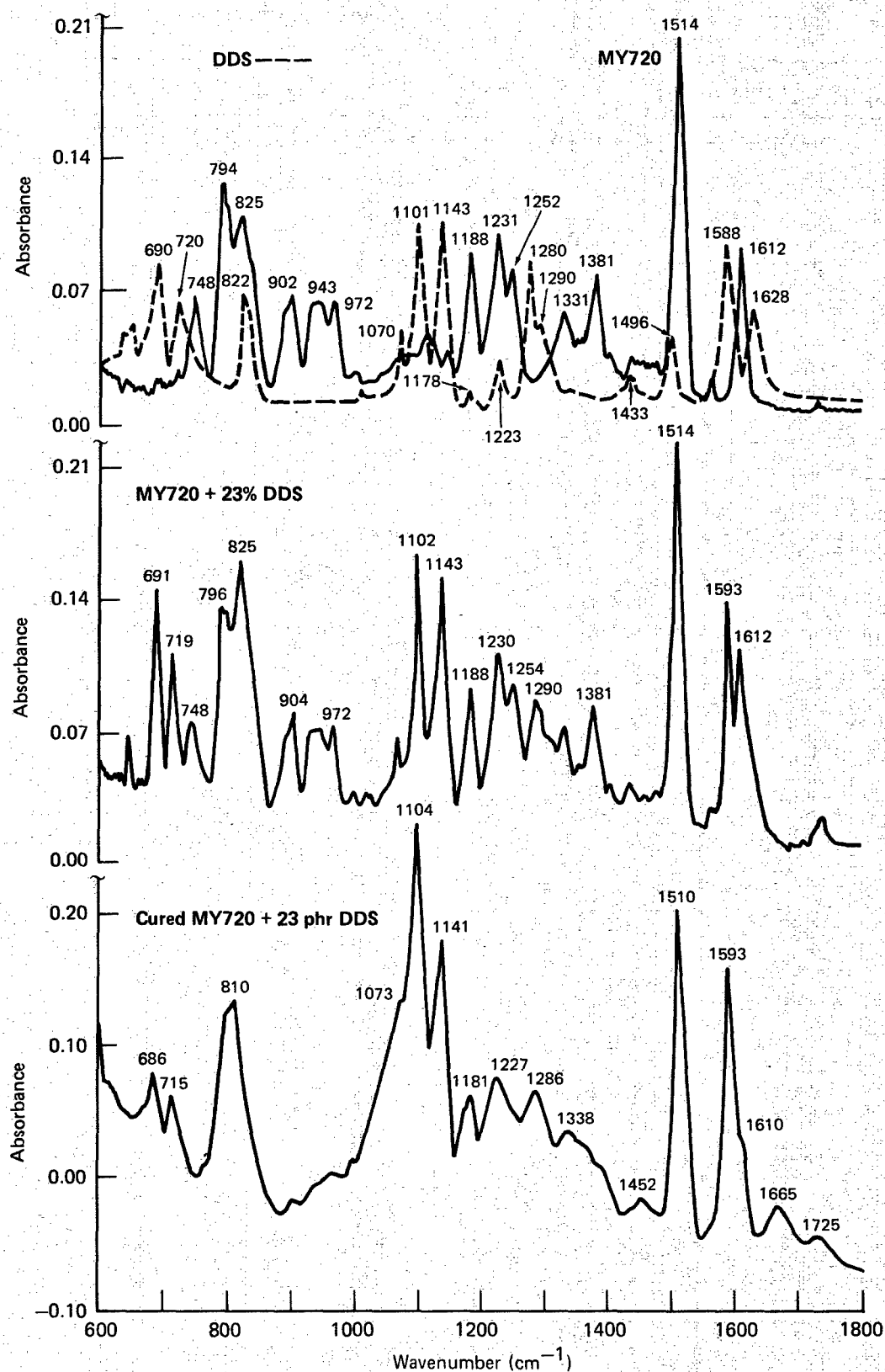




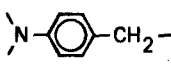
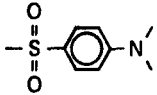
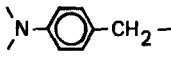
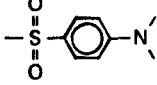

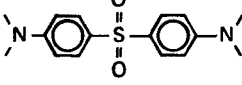

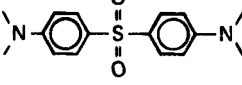
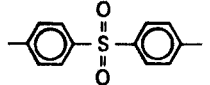
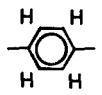
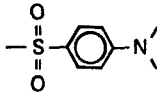
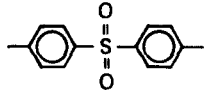


Figure 4 Internal reflection FT-IR spectra of DDS, MY720, and uncured and cured MY720 + 23 phr DDS mixture

**TABLE 2 ASSIGNMENT OF BANDS APPEARING IN THE INTERNAL REFLECTANCE INFRARED SPECTRA OF MY-720, DDS AND A CURED EPOXY SPECIMEN**

Frequency $\nu$ (cm <sup>-1</sup> )	Assignment	Position in the Network	Origin	Remarks
1725		Unknown	*	Product of thermoxidative reaction decreases as result of STM exposure
1665-75	Conjugated 	Unknown	*	Absorption at this frequency is characteristic for benzophenones and quinones
1640-56		Absorbed, free and H-bonded	*	
1622-8		Not present in the cured resin	DDS	Observed as negative band in curing sequence and in the pure DDS
1612	Benzene ring quadrant stretching		TGDDM	Less sensitive to mass of the substituents than the semicircle stretching band
1588	Benzene ring quadrant stretching		DDS	Less sensitive to mass of the substituents than the semicircle stretching band
1514	Benzene ring semicircle stretching (para subst)		TGDDM	Shifts to lower frequencies during curing and post-curing. This shift reverses as a result of exposure to STM
1496	Benzene ring semicircle stretching (para subst)		DDS	Not intense as the 1514 cm <sup>-1</sup> band
1280	$\nu$ asym  stretch		DDS	Heavily overlapped and considerably less intense than the $\nu$ sym band at 1141 cm <sup>-1</sup>
1135-46	$\nu$ sym 		DDS	Unobscured, valuable for diagnosis of changes, strong, appearing in most difference spectra, decreases upon absorption of water
1101-6	$\nu$ C - S		DDS	Strong, appearing in most difference spectra, decreases upon absorption of water
904	Oxirane ring	Not present in the cured resin	** TGDDM	
822-5 798	Two adjacent H wag (p-disubstituted benzene)		DDS TGDDM	Frequently appearing in difference spectra, valuable for establishing direction of the curing changes
715-20	Suspected to originate in benzene in-plane quadrant bending		DDS	Increases as a result of STM decreases in curing, valuable for direction of changes
686-91	$\nu$ sym C-S-C or quadrant in-plane bending of benzene		DDS	In both cases of assignment this band would be mass sensitive. STM causes an increase and curing causes a decrease

\*Band not present in the spectra of DDS and MY-720

\*\*Not present in the spectra of the cured resin

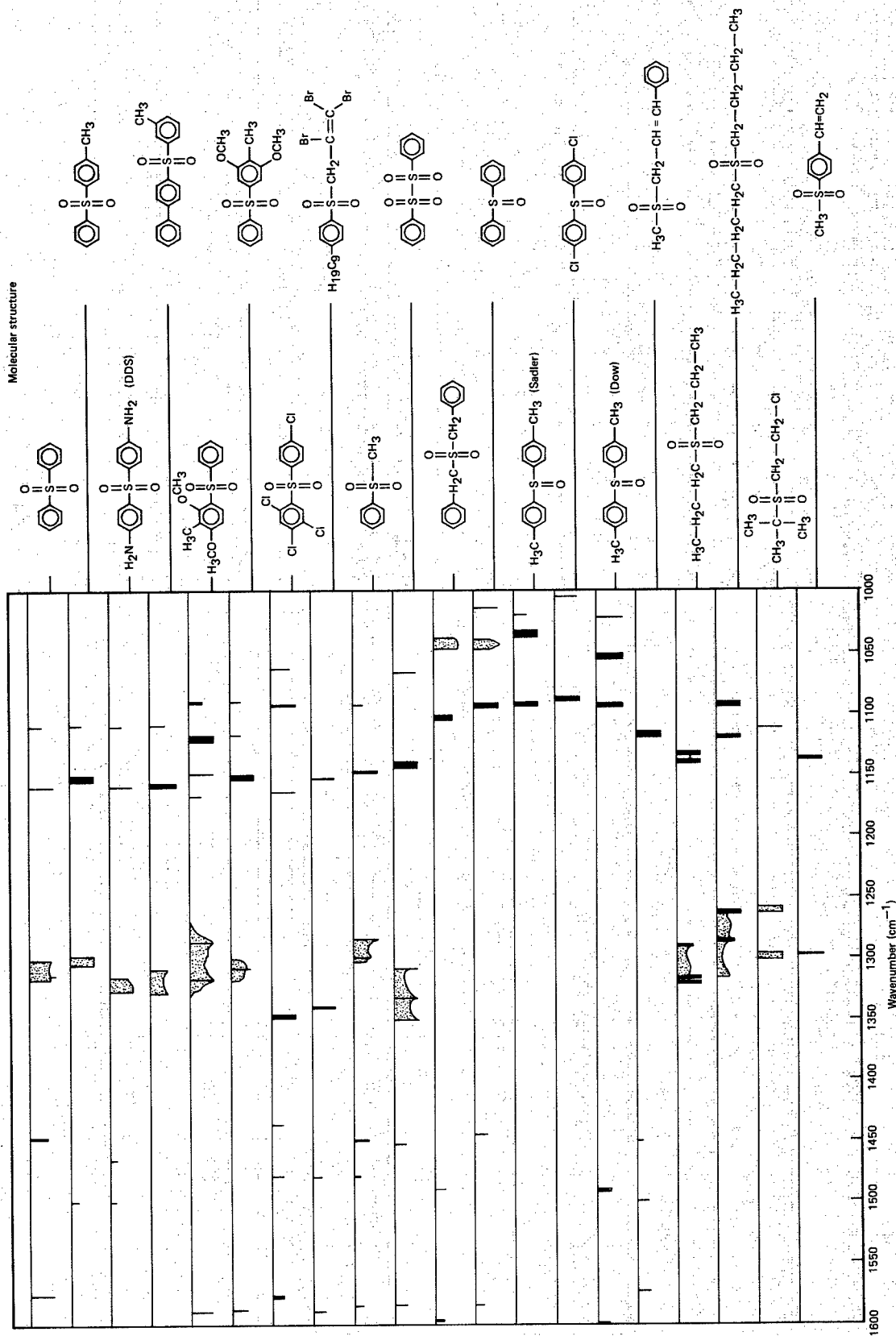


Figure 5 Selected infrared absorbance bands in organic compounds containing a sulfone group

The following sections describe the objectives, results, and conclusions of each series.

Acid/Base Immersion and STM Series - The catalytic effect of acids and bases on hydrolytic reactions is a well known phenomenon. Therefore, the possible effect of acidic or basic impurities present on the surface of the graphite fibers or in the starting materials must be considered.

The acid/base immersion and STM exposure series was performed to determine if contact with acidic or basic impurities affects the susceptibility of the epoxy resin to the STM environment. The experiments performed as part of this series are summarized in Table 1 and include a total of nine specimens: five immersed in solutions of pH 3-12 and four controls exposed to STM, ST, TM and T without any contact with acidic or basic solutions.

The difference FT-IR spectra representing after-minus-before immersion of five epoxy specimens to aqueous solutions of pH 3, 5, 7, 9, and 12 are shown in Figure 6. It can be concluded from this figure that, in general, immersion to acidic and basic solutions (followed by drying) does not induce major infrared spectral changes. However, this figure seems to indicate a slightly stronger effect of the acidic than the basic solutions. The superimposed difference spectra representing after-minus-before exposure of the acid/base-immersed specimens to the STM environment are shown in Figure 7. The features observed in these spectra are remarkably reproducible. All spectra show the small positive doublet at 690 and 717  $\text{cm}^{-1}$ . From these spectra it becomes obvious that immersion of the specimens to acidic or basic solutions does not alter their susceptibility to the STM.

Exposure to SM Combined with Thermal Spiking (TS) - The long-term ambient environment of aircraft with SNM composite components includes the elements of stress and moisture, while the short-term extreme conditions occurring during supersonic flight include rapid aerodynamic heating. Therefore, to simulate the long-term ambient and the short-term extreme environments of supersonic fighter aircraft, epoxy specimens were exposed to the SM environment at room temperature and thermally spiked as schematically shown in Figure 3. The difference FT-IR spectra representing after-minus-before exposure of two specimens to the SM plus TS along with difference spectra of the two control



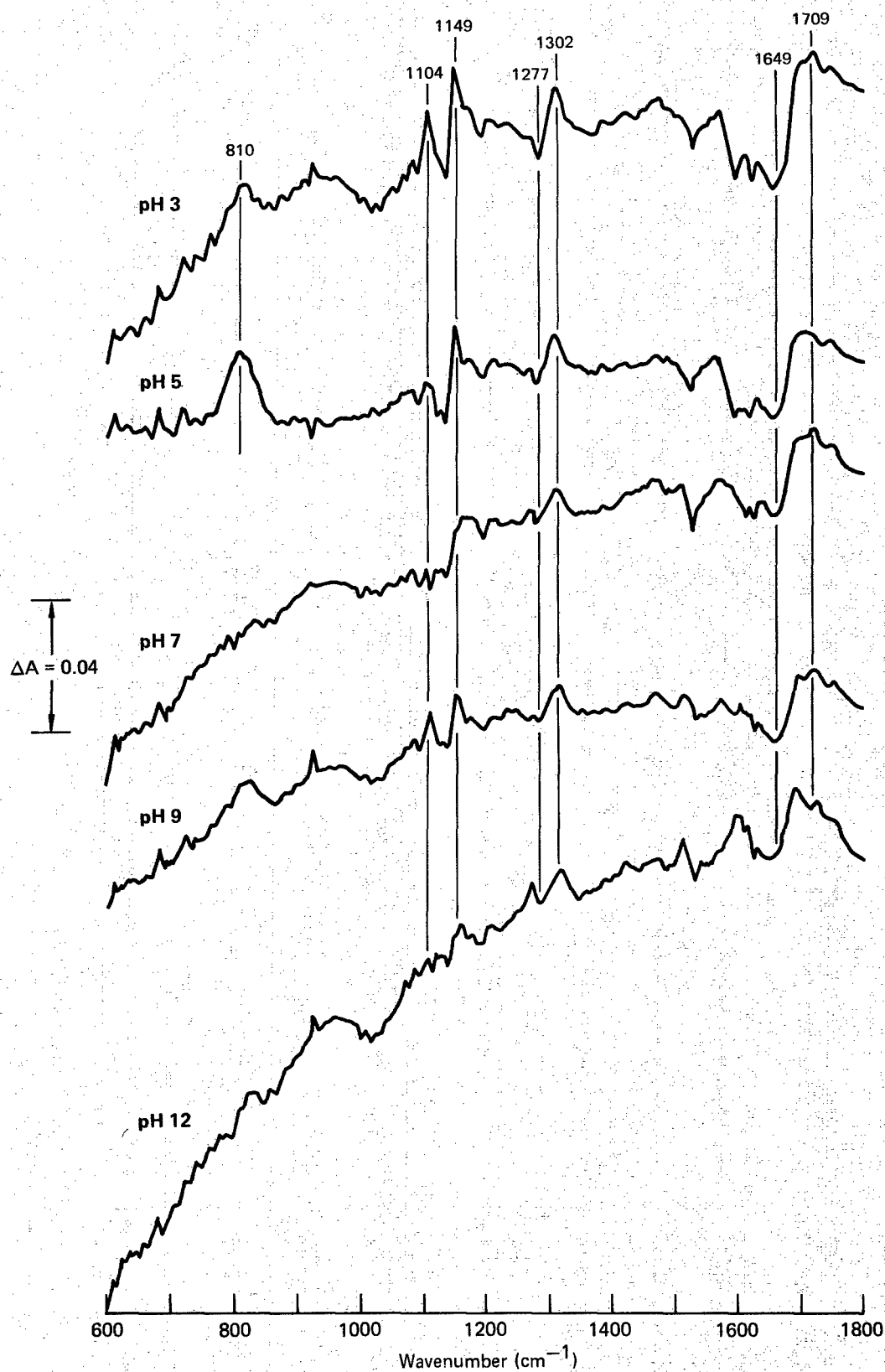
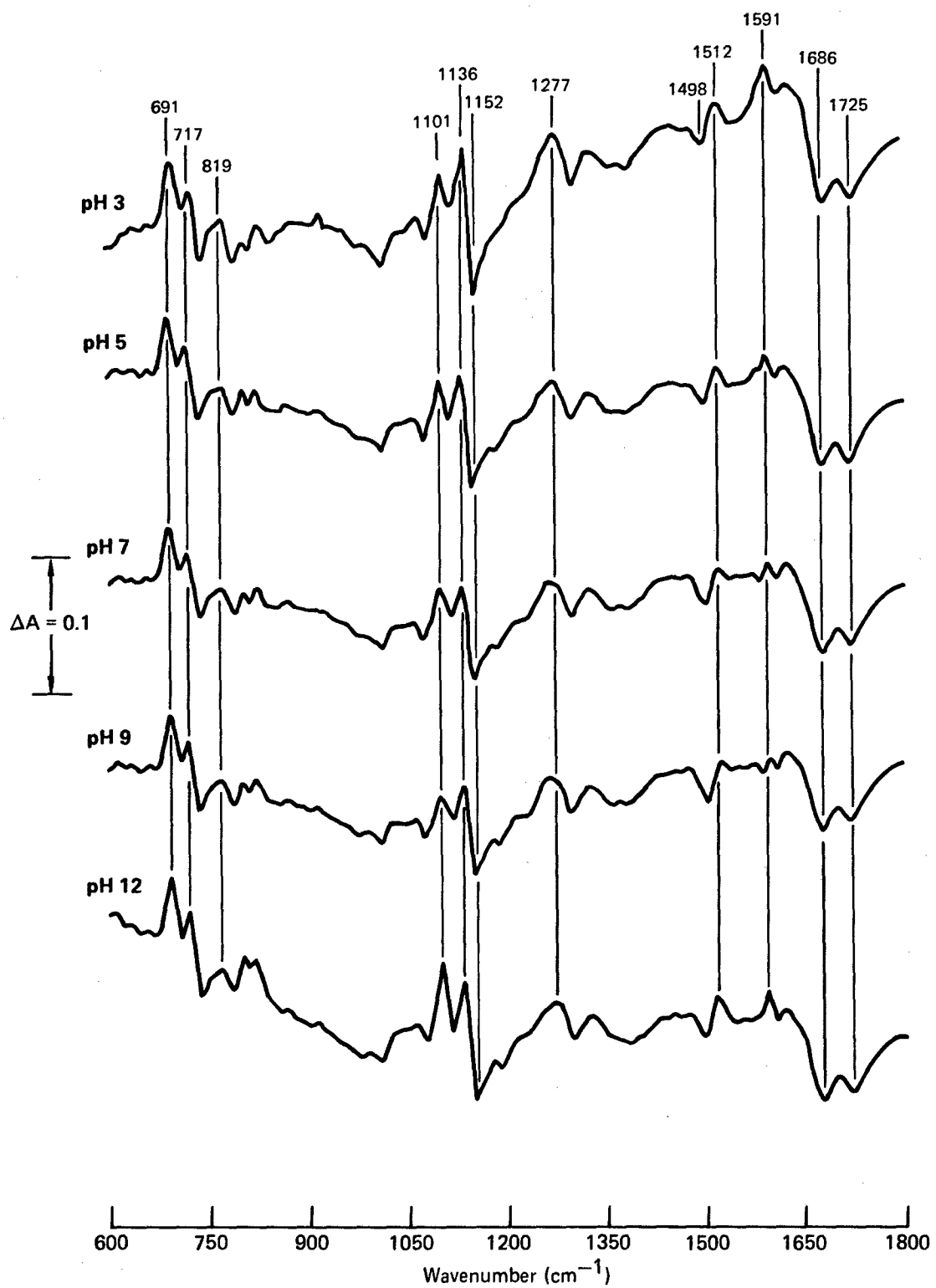


Figure 6 FT-IR difference spectra following immersion in aqueous solution with pH values of 3, 5, 7, 9, and 12



**Figure 7** Difference FT-IR spectra of samples exposed to STM following immersion in aqueous solutions with pH values of 3, 5, 7, 9, and 12

specimens exposed to the SM and M environments are shown in Figure 8. These spectra indicate that the main changes induced by SM plus TS resemble the changes induced by exposure to ST which are characterized mainly by occurrence of post-cure reactions. The spectral features which indicate this effect are the appearance of the negative sulfone doublet at 1104 and 1141-3  $\text{cm}^{-1}$ , the weak but noticeable negative doublet at 690 and 717  $\text{cm}^{-1}$ , and the unique pattern of the 1498-1512  $\text{cm}^{-1}$  benzene ring semicircle stretching band.

The positive 1660-4  $\text{cm}^{-1}$  band which also appears in all ST minus before-exposure difference spectra, which we tentatively assigned to an unknown conjugated carbonyl (Table 2), is undoubtedly a product of thermooxidative reaction which takes place to approximately the same extent in both the thermally spiked and unspiked specimens. The overall similarity of the thermally spiked and unspiked samples can be attributed to the drying stage at 90°C (Table 1) which follows the exposure to all three environments (SM plus TSM, SM, and M). The only spectral differences between the spiked and unspiked specimen appear in the 780-850  $\text{cm}^{-1}$  region. These differences are relatively minor but could eventually prove to contain useful information. In conclusion, thermal spiking of moisture-containing specimens to 100° and 135°C does not seem to induce any major changes relative to moisture-containing specimens exposed to the same stress but thermally unspiked.

Establishment of an Infrared Direction of Chemical Changes in Late Stages of Curing - As indicated earlier in this report, one of the ingredients of our approach developed to circumvent the complexity of the problem is the establishment of direction for the observed chemical changes occurring during the late stages of curing. During late stages of curing, the epoxy network resembles closely the network of a resin which has undergone the complete curing cycle. Therefore, the chemical changes occurring during post-curing reactions can be recognized and distinguished from changes induced by bond cleavages. The difference spectrum representing the FT-IR spectrum obtained after curing for 60 min at 150°C and 135 min at 177°C minus the spectrum obtained after curing for 60 min at 150°C and 60 min at 177°C is shown in Figure 9.

This internal reflectance difference spectrum is unique in comparison to all the other internal reflectance FT-IR spectra recorded during this study in that the specimen which was cured directly on the plate remained in the

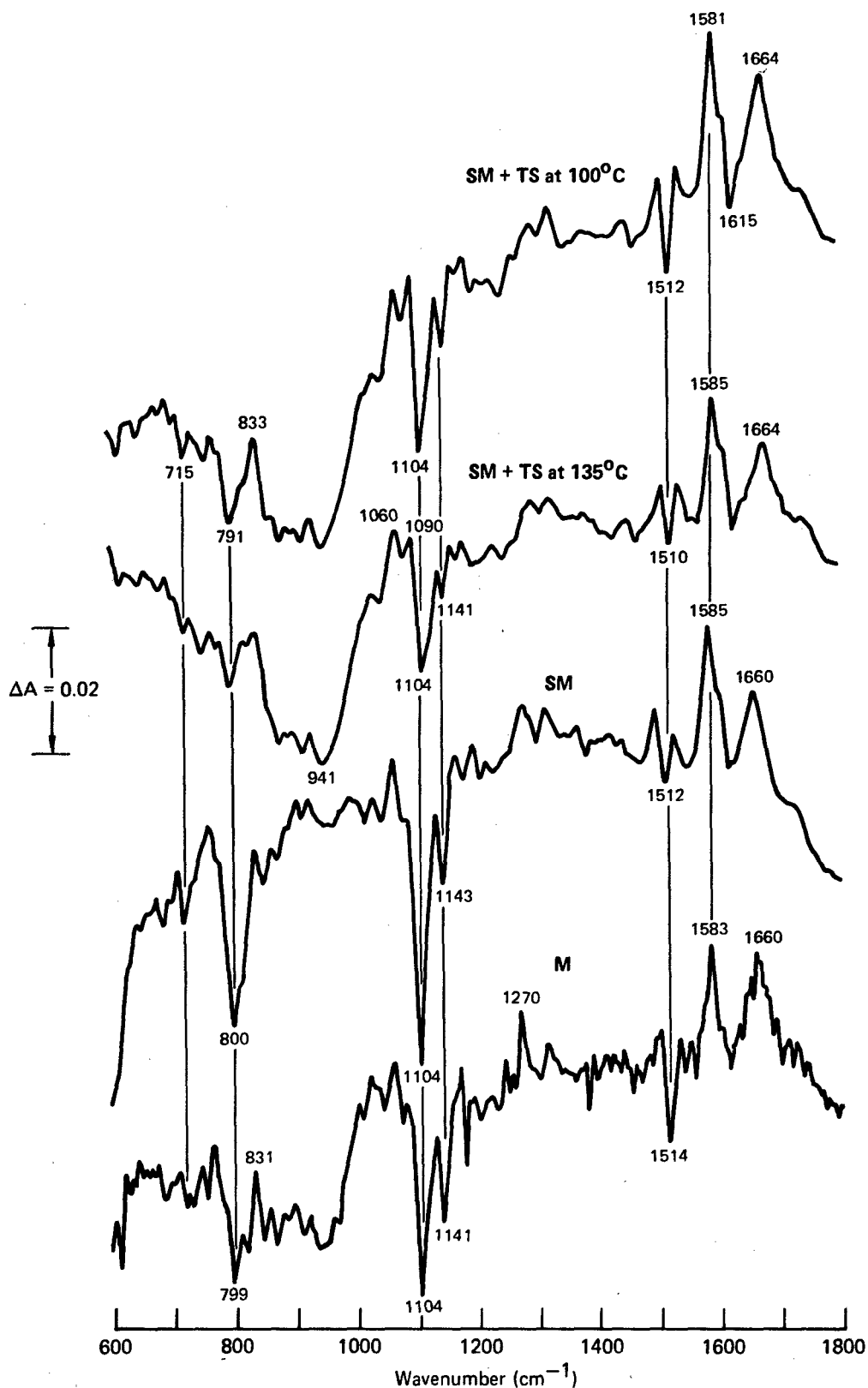


Figure 8 Difference FT-IR spectra representing after-minus-before exposure of two epoxy specimens to SM combined with thermal spiking (SM+TS) and two specimens to the SM and M environments

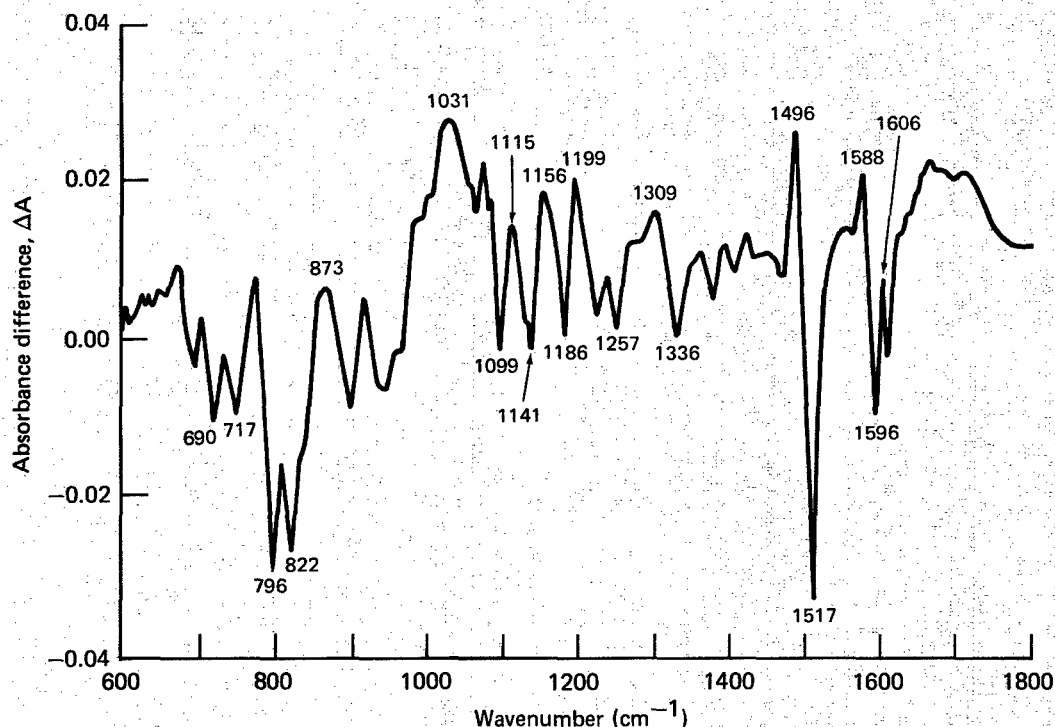


Figure 9 Difference FT-IR spectrum of late stages of curing representing 195 min cure minus 120 min cure

same degree of contact while both spectra were recorded and thus could be directly subtracted without use of scaling factors.<sup>5</sup> The observed changes therefore have both a quantitative and a qualitative meaning. Starting with the higher frequency bands, the most important spectral features which comprise a distinct direction of change characteristic of late curing are:

- 1) The frequency shift of the benzene semicircle stretching band from 1514 to 1495  $\text{cm}^{-1}$ ,
- 2) Decrease of the sulfone bands at 1101 and 1141  $\text{cm}^{-1}$ ,
- 3) Decrease of the 823-5  $\text{cm}^{-1}$  originating from adjacent aromatic H wagging,
- 4) Decrease of the 690, 717-9  $\text{cm}^{-1}$  doublet.

The usefulness of the direction of changes concept can be illustrated by comparing the spectral changes observed in Figure 9 with those observed in difference spectra of specimens exposed to the STM environment. Such comparison is provided in Figure 10 where the difference spectrum shown in Figure 9 is superimposed with two difference spectra representing after-minus-before exposure of two post-cured specimens to the STM environment.

The two STM spectra exhibit spectral changes in the opposite direction of the curing spectrum in all four of the characteristic regions of the spectrum

outlined earlier. The shift of the benzene semicircle stretching band in the opposite direction is visually easy to detect even in weak difference spectra. The increase of the sulfone bands is also highly visible. Note that the 1135-45  $\text{cm}^{-1}$  synthetic stretch band of the sulfone group seems to exhibit a frequency shift as well as positive direction upon exposure to STM.

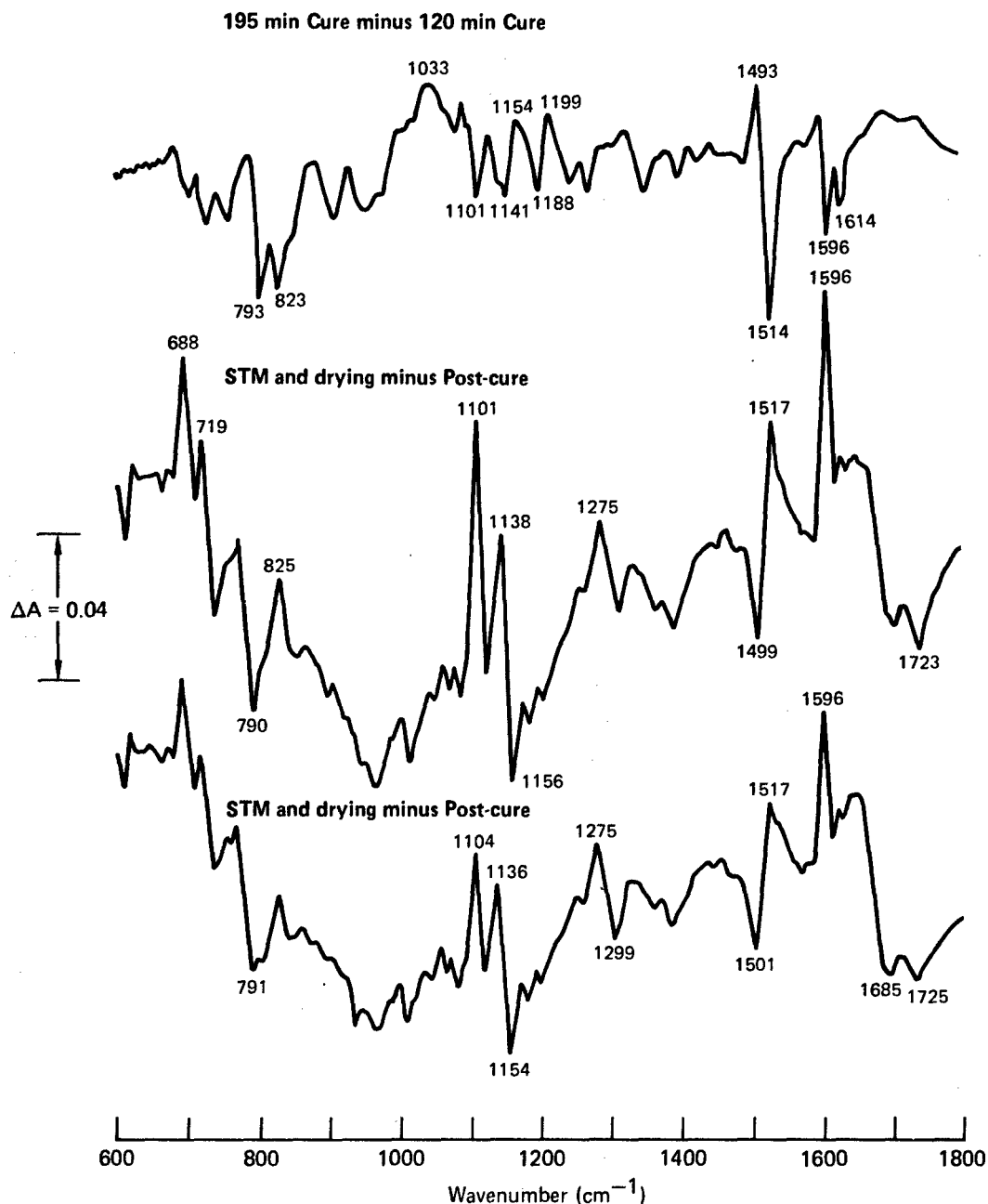


Figure 10 Superimposed difference spectra of late curing stage spectrum shown in Figure 9 and two spectra representing after-minus-before exposure of two post-cured specimens to STM

Although less dramatic, the  $823\text{--}5\text{ cm}^{-1}$  band appears strong enough to re-enforce a direction established by the other bands. Finally, the positive doublet at  $690$  and  $717\text{ cm}^{-1}$ , which at times is too weak to be noticed, exhibits remarkable consistency in all STM spectra.

Post-Cure Heating Followed by Exposure to STM - Since enhancement of post-cure reactions are postulated to be one of the important chemical effects of moisture<sup>4,5</sup>, it was assumed that the degree of post-cure can affect the susceptibility of the resin to the STM environment. Epoxy specimens were therefore post-cured at  $177^\circ$ ,  $185^\circ$ , and  $200^\circ\text{C}$  (Table 1), and FT-IR spectra were recorded before and after post-curing. The difference spectra representing after-minus-before post-curing at these temperatures are shown in Figure 11. The spectral features observed in this figure indicate occurrence of curing reactions by the direction of the frequency shift of the benzene semicircle stretch vibration at  $1496\text{--}1512\text{ cm}^{-1}$  and by the negative  $800\text{ cm}^{-1}$  band.

The negative sulfone doublet which accompanies the late stages of curing is not observed here, and the  $1144\text{ cm}^{-1}$  sulfone symmetric stretch vibration appears positive in all three spectra while the  $1102\text{--}4\text{ cm}^{-1}$  band appears partially obscured by the unusual broad negative band at  $1060\text{ cm}^{-1}$ . A speculative explanation for this reversal of the  $1144\text{ cm}^{-1}$  sulfone band attributes it to the removal of residual water molecules from the network thus freeing a fraction of the sulfone groups which were hydrogen bonded to these water molecules. An alternative explanation is to attribute the broad negative band to  $\text{H}_2\text{O}$  elimination through loss of a hydroxyl group by a mechanism known to occur in epoxy resins as the first stage of thermal degradation.<sup>12</sup> This hypothesis agrees with the presence of the broad negative band at  $1060\text{ cm}^{-1}$ . (Secondary alcohols generally present in epoxies do not absorb at frequencies as low as  $1060\text{ cm}^{-1}$ .) However, the true position of the broad negative band maxima is probably at  $1100\text{ cm}^{-1}$  but is obscured by the development of the positive sulfone band. A dotted line shown in Figure 11 illustrates the possible true shape of this broad negative band.

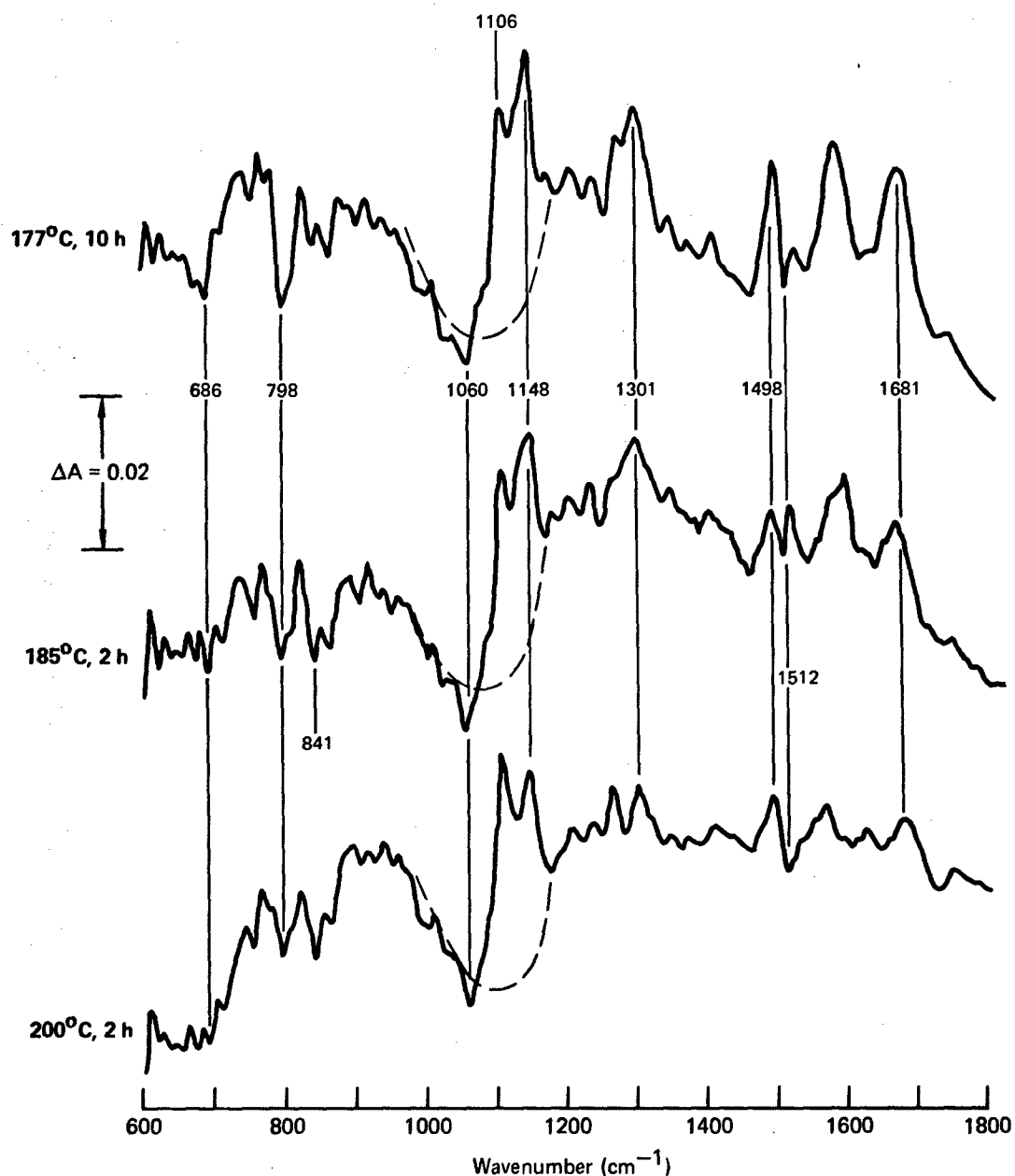


Figure 11 Difference FT-IR spectra representing after-minus-before post-cure heating of three specimens at 177°, 185°, and 200°C

Following post-cure heating, the specimens were exposed to the STM environment. The difference spectra representing after-STM minus after-post-cure are shown in Figure 12. Two of these difference spectra are also shown in Figure 10, and their features were discussed earlier. All three difference spectra exhibit the infrared features that we associate with changes characteristic of network degradation. The postulated mechanism responsible for the STM-induced changes is discussed in the following section.



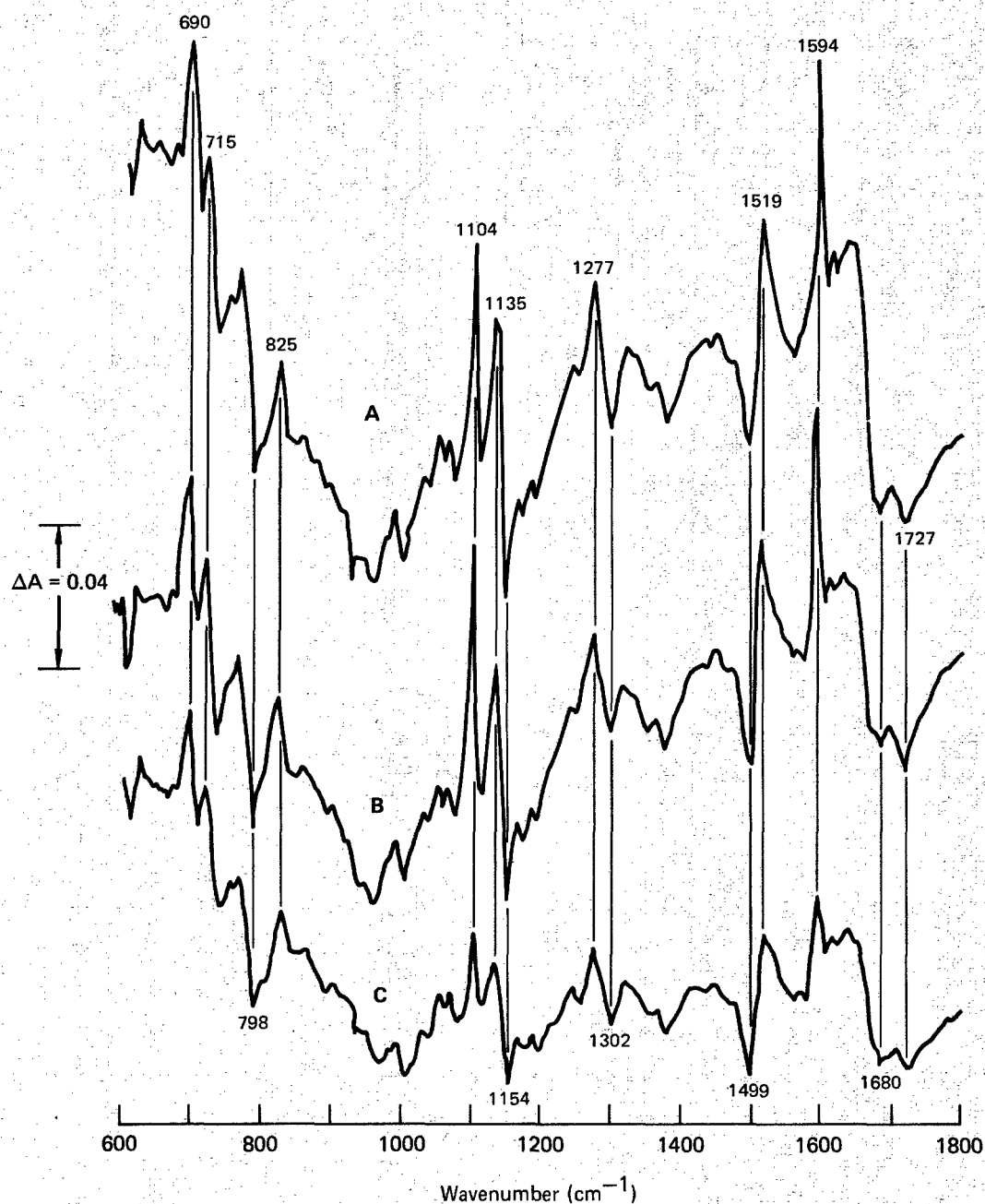


Figure 12 Difference FT-IR spectra representing after-STM minus after-postcure for specimens post-cured at A) 177°C (10 h), B) 185°C (2 h), and C) 200°C (2 h)

Spectral Effects of Absorbed Atmospheric Moisture - The capacity of the sulfone group to participate in hydrogen bonding is recognized.<sup>9</sup> On the molecular level, the plasticizing effect of water in epoxy resins is attributed to disruption of interchain hydrogen bonding by absorbed water molecules. In addition, we suspected that the sensitivity of the sulfone bands is related to

hydrogen bonding effects. It was, therefore, essential to investigate the spectral effects of absorbed atmospheric moisture on the various bands of the spectrum in general and on the sulfone bands in particular.

Epoxy specimens were allowed to absorb different weight percentages of moisture by exposure to 100% RH at room temperature. Spectra were recorded before and after the water absorption. The difference spectra representing after-minus-before absorption of 1.3, 1.5, 2.6, and 3.0 wt% water are shown in Figure 13. All spectra show substantial spectral effects. The positive  $1650\text{ cm}^{-1}$  band is attributed directly to the increase of water content. The highly diagnostic shift of the benzene ring semicircle band at  $1496\text{--}1512\text{ cm}^{-1}$  indicates a small change in the direction of further curing.

If this small change truly reflects a slight water-induced post-cure reaction occurring in the plasticized resin at room temperature, then the effect of water as a plasticizing catalyst for the post-cure reaction at elevated temperature<sup>4</sup> also occurs at lower temperatures. Such a room-temperature effect would most likely be limited to those post-cure reactions which can be facilitated by relaxation of internal stresses induced by the plasticizing effect of water. Absorbed moisture at room temperatures induces changes in the sulfone bands at  $1102$  and  $1135\text{--}46\text{ cm}^{-1}$ . The changes induced in these bands by absorption of 1.3 wt% water (Figure 13) along with the negative  $800\text{ cm}^{-1}$  band and the diagnostic shift mentioned earlier strongly resemble the difference spectrum representing ST minus before-exposure for  $T = 150^\circ\text{C}$  shown in Figure 14. In both cases, the negative sulfone band at  $1102\text{ cm}^{-1}$  is larger than the companion band at  $1145\text{ cm}^{-1}$ . Since we have established earlier<sup>5</sup> that the main effect of exposure to ST is the post-cure reaction, this similarity offers additional proof of the suspected room-temperature, post-cure effect of water. As the water content increases to 2.6 wt%, the changes in the sulfone bands exhibit a reversal of their relative intensity. Here the  $1146\text{ cm}^{-1}$  band assigned to the symmetric stretch vibration is reduced more than the  $1102\text{ cm}^{-1}$  stretch vibration. Hydrogen bonding of water molecules to the oxygen atoms of the sulfone group is offered as an unconfirmed explanation for this observation.

Exposure of Epoxy Specimens to Elevated-Temperature ST Environments - In principle, all the ST experiments were conducted to provide the control needed to obtain the STM-minus-ST difference spectra which were expected to yield the

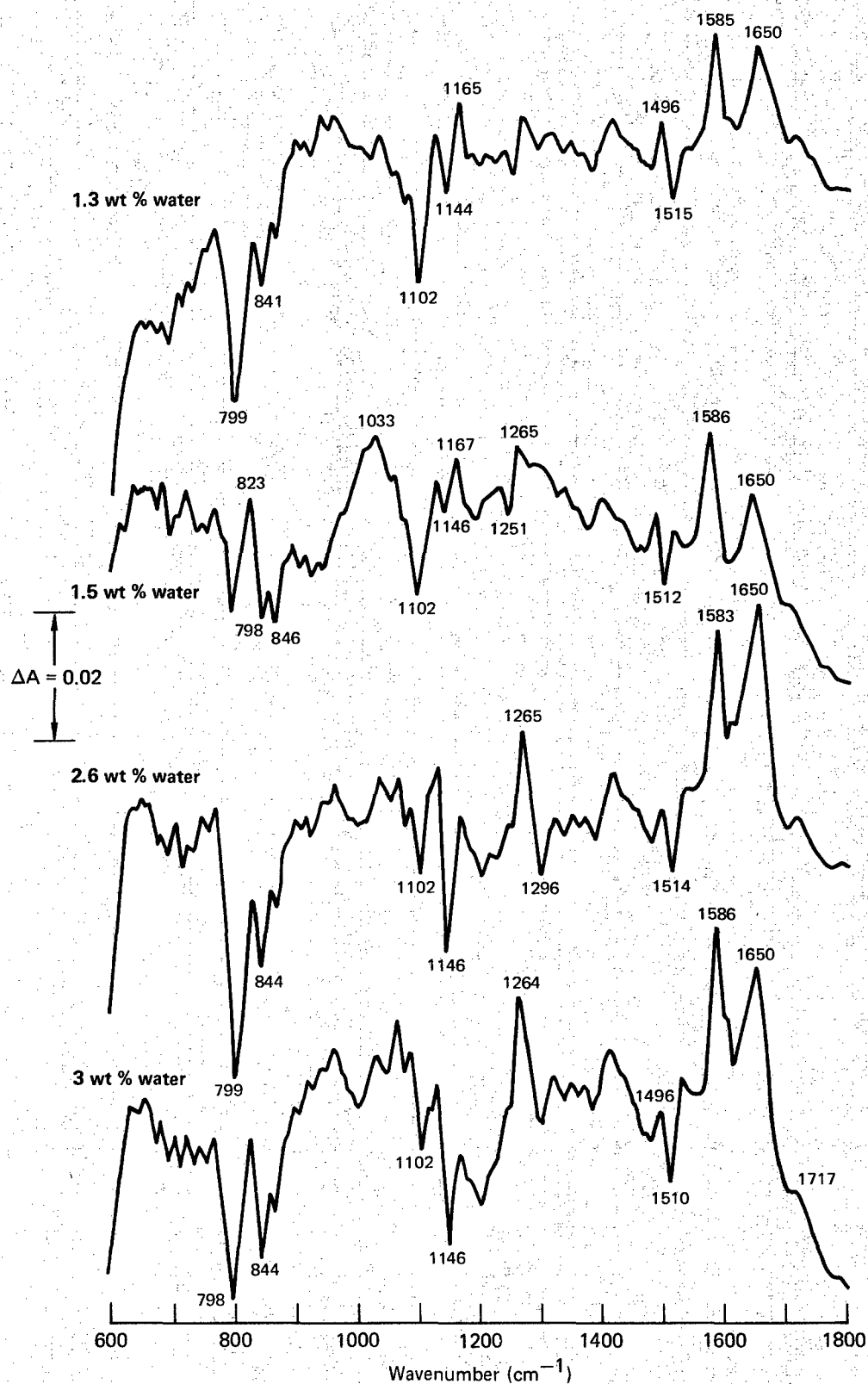
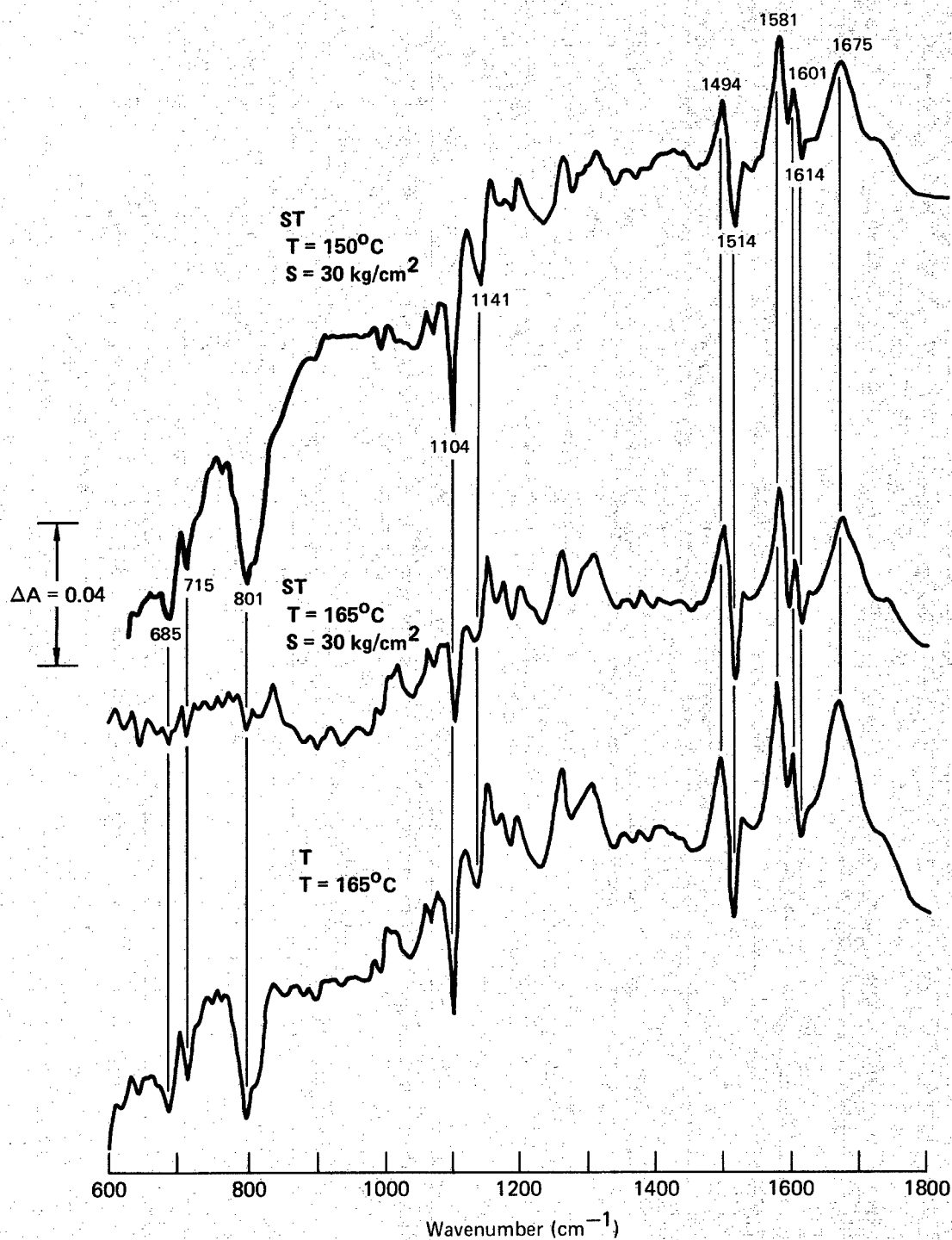


Figure 13 Difference FT-IR spectra representing after-minus-before absorption of 1.3, 1.5, 2.6, and 3.0 wt % water for four different epoxy specimens

net effect of moisture on the chemical changes. Therefore, exposures to the ST environment were always performed at 135°C (which is the temperature for all STM experiments) and at the same stress levels used for the STM experiments. However, we recognized that as a consequence of the plasticizing effect of water, the molecular mobility in a moisture-saturated resin is greater than of a dry resin. Therefore, the chemical changes that depend on the extent of molecular mobility would progress further in an STM environment than in a ST environment. A series of experiments based on exposure of epoxy specimens to ST and T environments at temperatures higher than 135°C was conducted to determine the effect of stress on the chemical changes occurring in a dry resin at molecular mobilities comparable to those of a plasticized resin at 135°C. The difference FT-IR spectra representing after-minus-before exposure to the ST environment at 165°C are shown in Figure 14. All three spectra exhibit features which we associate with the expected post-cure reactions. The diagnostic 1512 to 1496  $\text{cm}^{-1}$  shift appears in all three spectra in a distinct and almost identical form. The negative sulfone doublet at 1102  $\text{cm}^{-1}$  and 1141  $\text{cm}^{-1}$  (with the 1102  $\text{cm}^{-1}$  band larger than the 1141  $\text{cm}^{-1}$  band) also appears in all three spectra. The absence of the 798-810  $\text{cm}^{-1}$  negative band in the 165°C ST minus before-exposure difference spectrum is likely to be a result of an experimental error or an unusual feature of this specimen. The difference spectrum representing ST-minus-T shown in Figure 15 does not exhibit spectral features of sufficient intensity to permit reliable detection of a net stress effect. It can be concluded that exposure of specimens to the ST environment at temperatures up to 30°C higher than the standard 135°C does not cause detectable stress effects.

Stress Effects in Exposure to the STM Environment - To determine the extent stress affects the observed chemical changes induced by the STM environment, a series of specimens was exposed to the STM environment at stress levels ranging from 0 to 90  $\text{kg/cm}^2$ . Difference FT-IR spectra representing after-minus-before exposure to the STM environment at stress levels of 0, 16, 30, 60, and 90  $\text{kg/cm}^2$  are shown in Figure 16. All spectra exhibit a remarkably similar pattern with spectral features with similar relative intensities; because of these features we conclude that tensile stress is not the factor responsible for the observed changes.



**Figure 14** Difference FT-IR spectra representing after-minus-before exposure of three epoxy specimens to ST environments at  $150^{\circ}\text{C}$  and  $165^{\circ}\text{C}$  and to the T environment at  $165^{\circ}\text{C}$

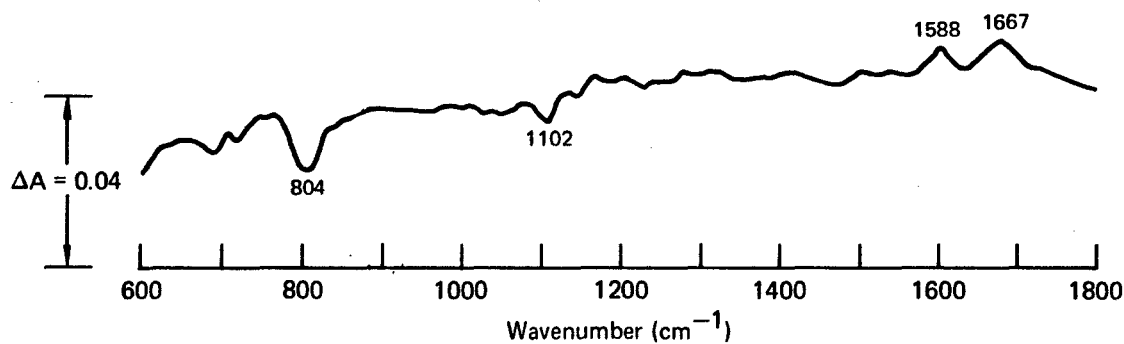


Figure 15 Difference FT-IR spectrum of two epoxy specimens representing ST-minus-T at 165°C

The Effect of DDS Concentration on the Susceptibility to the STM Environment - The possibility that the DDS concentration could alter the response of the epoxy resin to the STM environment through its effect on the network structure was investigated by exposing a series of specimens containing different percentages of DDS to the STM environment. The difference FT-IR spectra representing after-minus-before exposure to the STM environment of specimens containing 23, 27, and 35 parts per hundred (phr) DDS are shown in Figure 17. All three spectra exhibit similar features in the diagnostic regions defined earlier for the establishment of the direction of changes. These features represent the frequency shift in the 1500-1512  $\text{cm}^{-1}$  region of the positive sulfone bands at 1102  $\text{cm}^{-1}$  and 1139  $\text{cm}^{-1}$  and the positive doublet at 719 and 690  $\text{cm}^{-1}$ .

The differences in the  $\Delta A$  scales should be noted. These differences arise from differences in the overall intensities of the original spectra. For instance, the original before and after spectra of the specimen containing 23 phr DDS were more than twice the intensity of the original spectra of the specimens containing 35 phr DDS. The  $\Delta A$ 's are neutrally proportional to these differences in the intensities of the original spectra. It can be concluded from these observations that the general changes induced by the STM environment remain relatively constant for the 12 phr range of DDS addition studied in this experiment.

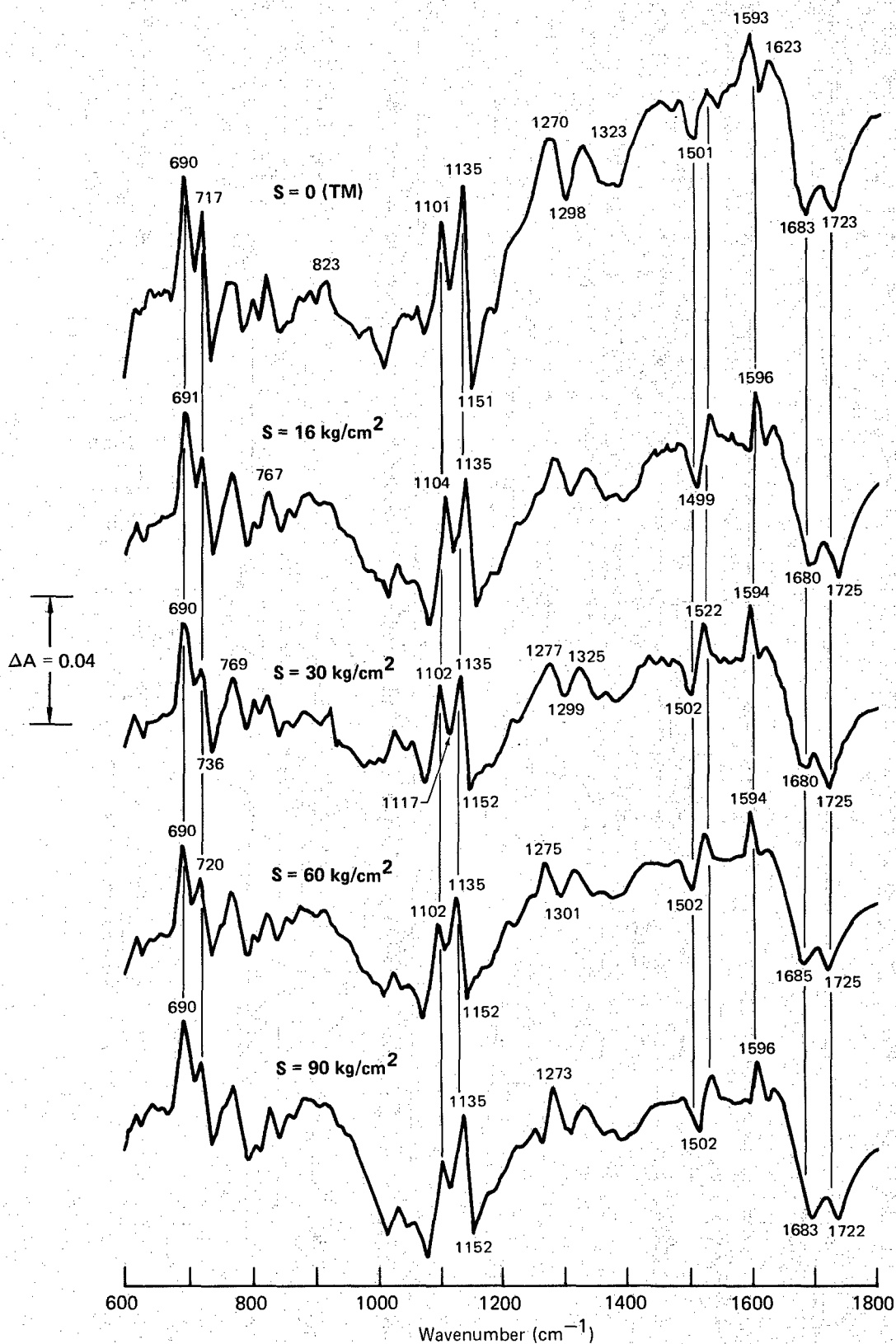


Figure 16 Superimposed difference FT-IR spectra which represent after-minus-before exposure of four epoxy specimens to the STM environment at stress levels of 0, 16, 30, 60 and 90  $\text{kg/cm}^2$

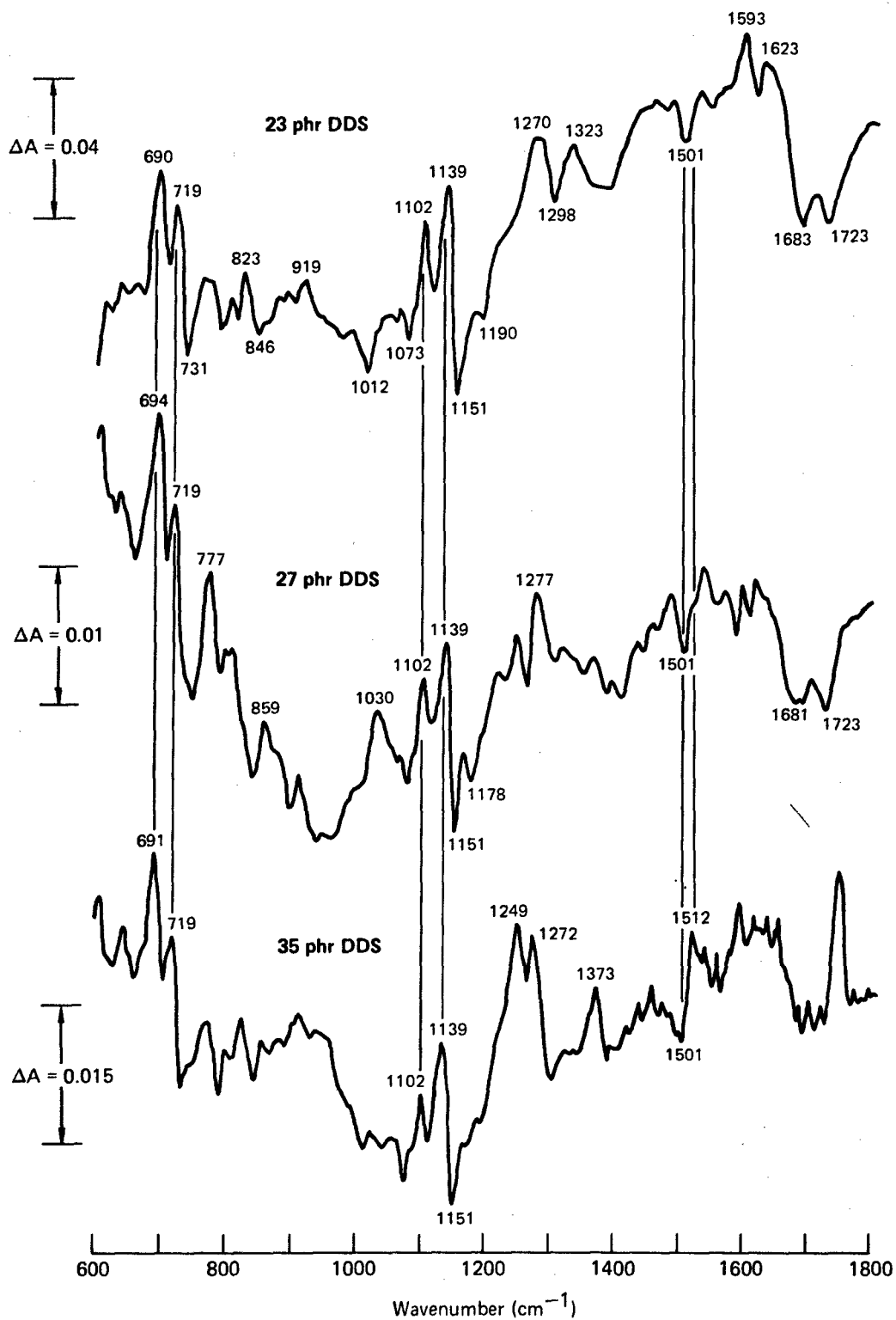


Figure 17 Superimposed difference FT-IR spectra which represent after-minus-before exposure to the STM environment of epoxy specimens containing 23, 27, and 35 parts per hundred (phr) DDS



Transmission Near-Infrared Measurements for Specimens Exposed to the STM and ST Environments - The successful near-infrared experiments conducted by Browning<sup>4</sup> with a dispersive infrared spectrometer indicated that FT-IR spectroscopy might provide additional information on the processes occurring during exposure to STM because of the greater sensitivity of the difference spectroscopy.<sup>5</sup> The transmission FT near-infrared spectra epoxy specimens containing different DDS concentrations were recorded before and after exposure to the STM environment.

Difference spectra representing after-minus-before exposure to the STM environments for specimens containing 17, 23, 27, and 35 phr DDS are shown in Figure 18. The negative  $4508\text{ cm}^{-1}$  band attributed to the epoxy group<sup>4,8</sup> appears in all four spectra shown in Figure 18, as well as a positive band at  $5200\text{--}5212\text{ cm}^{-1}$  which can be assigned to OH in water.<sup>4,8</sup> These data clearly indicate that for all four DDS concentrations, exposure to the STM environment induces a decrease in the number of residual epoxy groups.

The decrease in this band as function of cure was observed by Browning<sup>4</sup> for a specimen at different stages of cure ranging from 1-3 h at  $121^{\circ}\text{C}$  followed by 1 h at  $150^{\circ}\text{C}$  and 0.5 h at  $177^{\circ}\text{C}$ , and also for a specimen exposed to a  $150^{\circ}\text{C}$  underwater environment for 1 h. Browning also found that the decrease of the residual epoxy for the specimen exposed to  $150^{\circ}\text{C}$  underwater is accompanied by an increase of the rubbery modulus thus proving that the disappearance of the residual epoxy group is due to additional cure and not merely a result of epoxy hydrolysis producing a diol.

Of course, the possibility of such hydrolytic conversion of epoxy groups to diol cannot be excluded. Transmission FT near-infrared spectra of epoxy specimens exposed to STM at two different stress levels ( $16$  and  $90\text{ kg/cm}^2$ ) and to ST ( $16\text{ kg/cm}^2$ ) along with the spectrum of a control specimen were recorded to explore the possibility that the effect of stress might be detectable in the near-infrared. The difference spectra representing STM-minus-control for the two different stress levels and ST-minus-control are shown in Figure 19. The two STM difference spectra appear almost identical, indicating no detectable stress effect at near-infrared wavelengths. The ST-minus-control spectrum shows only a negligible reduction of the residual epoxy groups indicating that most observed changes in difference spectra ST minus before-exposure (Figure 14), which we attribute to post-cure reactions, represent mainly reactions which do not involve residual epoxy groups.

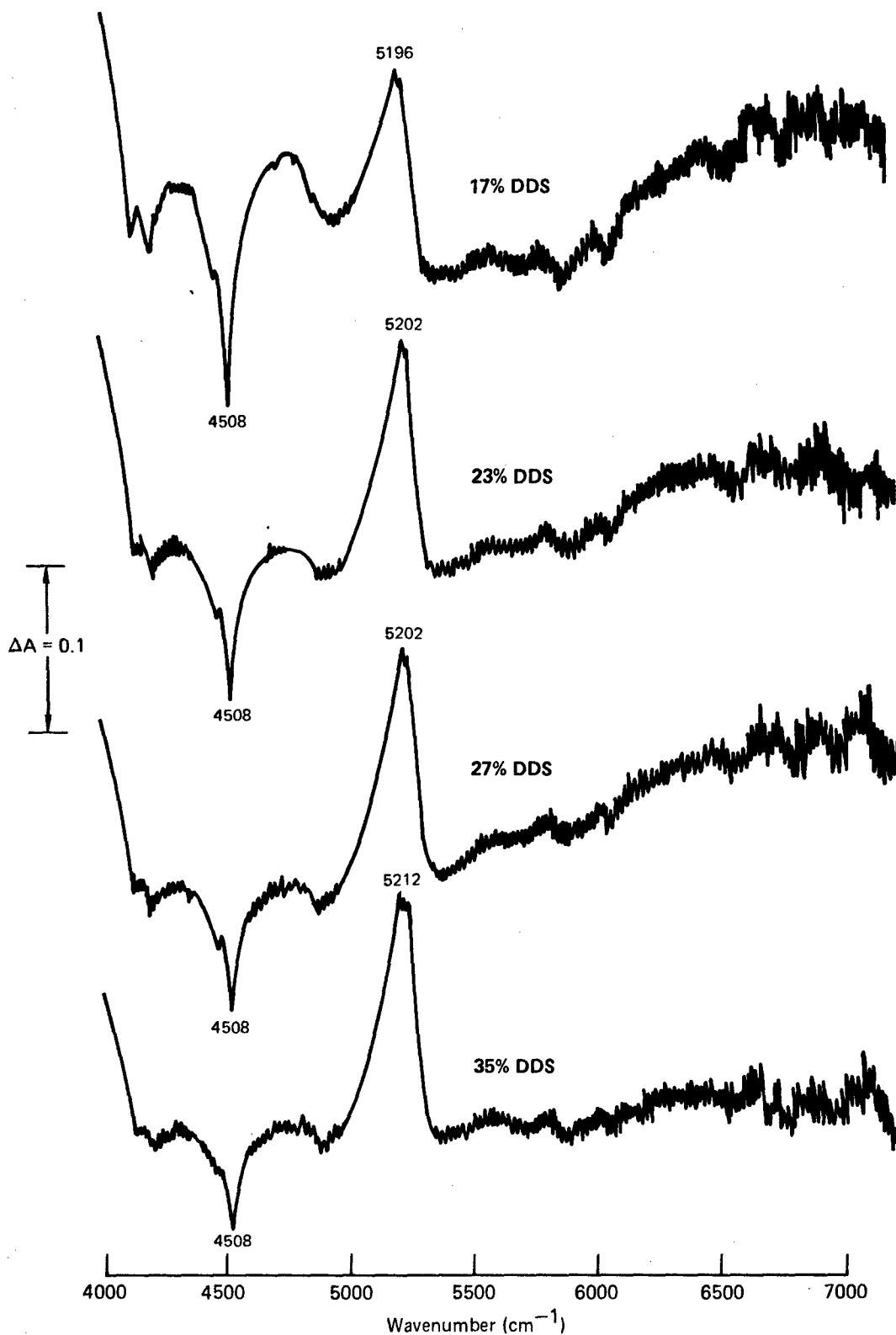


Figure 18 Near infrared transmission difference spectra representing after-minus-before exposure of four epoxy specimens containing 17, 23, 27 and 35 phr DDS to the STM environment

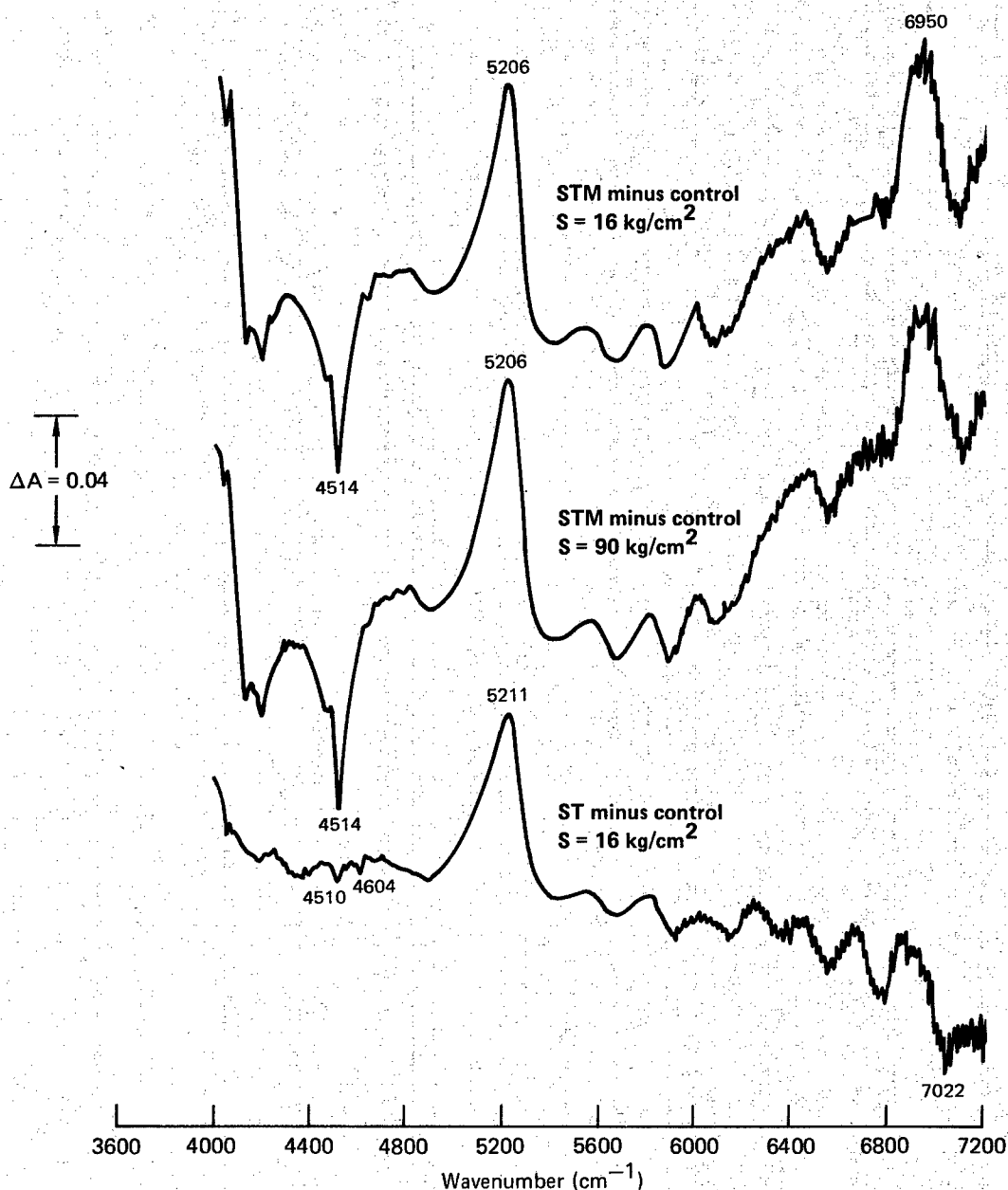


Figure 19 Transmission FT-near-IR difference spectra representing STM minus control for two different stress levels and ST minus control

#### 4. POSTULATED MECHANISMS RESPONSIBLE FOR THE OBSERVED SPECTRAL CHANGES

The objectives, conclusions, and main spectral features of the different series of experiments are summarized in Table 3.

Based on these conclusions and considering the limitations of internal reflectance spectroscopy, the following qualitative mechanism for the irreversible chemical changes induced by the specific environments is proposed:

**TABLE 3 SUMMARY OF OBJECTIVES, RESULTS AND SPECTRAL FEATURES OF THE MAIN EXPERIMENT SERIES**

Experiment Series	Objectives	Spectral Features	Results and Conclusions
Acid/Base Immersion and STM Exposure	Determine if acidic or basic impurities, likely to be present on the fiber surface, affect hydrolytic stability	STM minus after acid or base immersion difference spectra appear identical to STM minus before-exposure spectra (Fig. 7)	Immersion of specimens in aqueous solutions (pH 3-12) prior to STM exposure does not alter the susceptibility to STM
Thermal Spiking and exposure to SM at room temperature	Simulate aircraft environment, i.e., long-term runway absorption of moisture and short thermal spike from supersonic dash	Both spiked and unspiked specimens show decrease of $1104\text{ cm}^{-1}$ and $1143\text{ cm}^{-1}$ sulfone bands and broadening of the $1512\text{ cm}^{-1}$ band. (Fig. 8)	Specimens exposed to SM and spiked three times at $100^{\circ}$ and $135^{\circ}\text{C}$ do not show dramatic spectral differences in comparison to specimens exposed to SM only
Curing Sequence	Determine the spectral changes that take place during late stages of curing and correlate with spectral features induced by STM	Decrease of $690$ , $1102$ , $1141\text{ cm}^{-1}$ bands and shift of aromatic $1517\text{ cm}^{-1}$ band to $1496\text{ cm}^{-1}$ (Fig. 9)	The extent and direction of intensity changes in the mass sensitive $690\text{ cm}^{-1}$ band, the sulfone bands and the shift of the aromatic band were determined and used as a basis for the proposed mechanism
Post-cure heating and exposure to STM	Determine effect of posture on the chemical susceptibility to STM	Spectra of STM minus posture closely resemble STM minus before-exposure spectra (Fig. 12)	Post-cure does not significantly alter the chemical susceptibility to the autoclave STM
Stress effects in exposure to STM	Determine to what extent stress affects the observed chemical changes induced by STM	Spectra of STM before-exposure at different stress levels and TM minus before-exposure are almost identical (Fig. 16)	The observed STM changes originate in the swelling stresses not in the external tensile stress applied
Effect of DDS content	Investigate the effect of DDS concentration on the chemical susceptibility to STM	Spectral patterns of STM minus before-exposure for specimens of different DDS content are very similar (Fig. 17)	DDS content does not alter the mechanism responsible for the observed infrared features
Moisture content effects	Determine the spectral effects of absorbed atmospheric moisture at room temperatures	Increase of water content induces a decrease of the $1104$ , $1145$ and $798\text{ cm}^{-1}$ bands and a frequency shift in the $1500\text{ cm}^{-1}$ band (Fig. 13)	Hydrogen bonding between water molecules and the sulfone group leads to a decrease in the sulfone band intensities. Limited post-cure reactions occur because of relaxation of internal stresses
Near infrared transmission spectra	Obtain spectral evidence for stress-induced changes	STM minus before-exposure spectra show decrease of residual epoxy at $4512\text{ cm}^{-1}$ ; ST minus control shoes negligible decrease at $4512\text{ cm}^{-1}$ (Figs. 18, 19)	Near-infrared does not provide detectable spectral features which can be attributed to the effect of stress

- 1) Exposure of epoxy specimens to the autoclave STM and TM environments leads to bond cleavage in the aliphatic portions of the epoxy network. These observed bond cleavages are induced by swelling stresses and are independent of the external tensile stress at least for the surface layer examined by internal reflection spectroscopy.
- 2) Exposure to the autoclave STM also leads to enhancement of the post-cure reaction of residual epoxy groups by increasing molecular mobility.
- 3) The extent of post-cure reactions induced by the STM and TM environments appears to be less than the bond cleavage induced in the network by these environments.
- 4) Infrared spectral evidence suggests that absorption and desorption of water by epoxy specimens at room temperatures induces limited post-cure reactions through relaxation of internal stresses thus bringing reactive moieties closer.
- 5) No significant spectral evidence could be directly linked to the effect of external tensile stress on the observed changes.
- 6) The mechanism responsible for the decrease of the intensities of the sulfone bands at  $1126\text{ cm}^{-1}$  and  $1135\text{--}46\text{ cm}^{-1}$  observed during curing probably reflects an alignment of part of the DDS molecules participating in the curing so that they form hydrogen bonds which inter-chain neighboring OH groups.<sup>13</sup> Part of the reacted DDS sulfone groups do not enter into such hydrogen bonding interactions and are the first to form hydrogen bonds with absorbed water molecules.
- 7) The bond rupture induced by STM and TM releases certain segments of the network which vibrate (i.e., absorb infrared radiation) at frequencies and with intensities characteristic of their unreacted or monomeric state. Thus observed band intensity increases, and frequency shifts characteristic of bond cleavage exceed the changes characteristic of the post-cure process.
- 8) The tentatively postulated rupture of the carbon-sulfur bond suggested in the first phase of this study<sup>5</sup> as one possible explanation for the observed changes in the sulfone bands appears incompatible with the experimental evidence obtained in this study. The observations on the changes of the sulfone bands at room temperature

clearly indicate a hydrogen bonding mechanism, thus eliminating the need to invoke the thermal degradation model proposed by Levantovskaya<sup>14</sup> for polysulfone.

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